

REMARKS

Claims 7-16, 18-26 and 30-32 are active. While a clean copy of claims is provided for the convenience of the Examiner, no amendments have been made. No new matter has been added. Favorably consideration of this amendment and allowance of this application is respectfully requested.

Rejection—35 U.S.C. §112, first paragraph

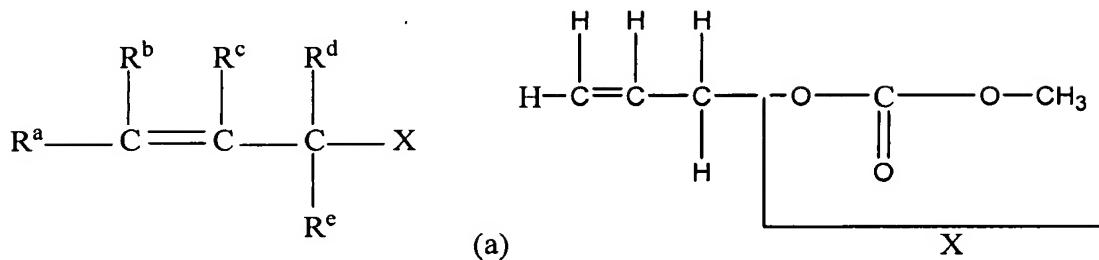
Claims 7-16, 18-26 and 30-32 were rejected under 35 U.S.C. 112, first paragraph, as lacking adequate written description for “is a compound in which X in the first allyl compound is substituted with AO”. The Examiner has indicated that “The AO group is only used in reference to the oxygen nucleophilic agent”, however, it is not necessary for the specification to explicitly describe the exact wording “the second allyl compound is a compound in which X in the first allyl compound is substituted with AO” when that concept is clearly described.

Under U.S. practice, a claim term need not be literally described in the specification.

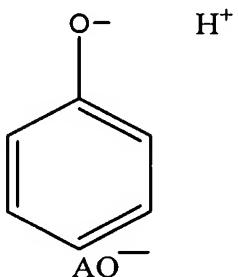
The test for determining compliance with the written description requirement is whether the disclosure of the application as originally filed reasonably conveys to the artisan that the inventor had possession at that time of the later claimed subject matter, **rather than the presence or absence of literal support** in the specification for the claim language (emphasis added), In re Kaslow, 217 USPQ 1089 (Fed. Cir. 1983).

Here, the alleged new matter--the concept of substituting the leaving group (X) in the first allyl compound (allyl-X) with the group AO in the oxygen nucleophilic compound (AO-H) to obtain a second allyl compound (allyl-AO)--is clearly disclosed. Moreover, this aspect of the invention is actually exemplified in Example 1 on page 59 of the specification:

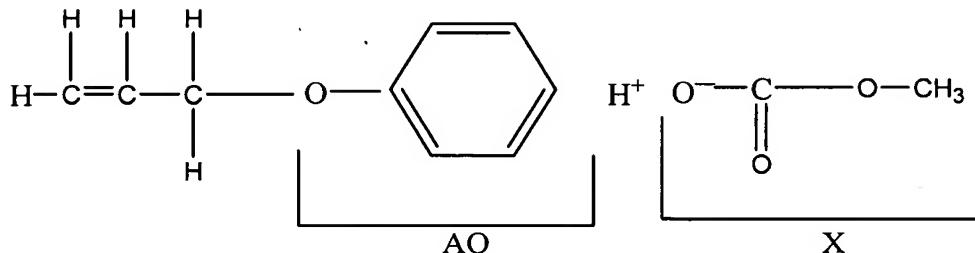
First allyl compound = allyl methyl carbonate:



Oxygen nucleophilic agent = phenol, where AO^- and H^+ are shown below:



2nd allyl compound = allyl phenyl ether



Accordingly, the Applicants respectfully request that this new matter rejection be withdrawn.

Rejection—35 U.S.C. §102

Claims 7-9, 11, 14, 15, 18, 22-24 and 30-32 were rejected under 35 U.S.C. 102(b) as being anticipated by Trost, U.S. Patent No. 4,051,157. The Applicants incorporate their prior arguments with respect to the differences between the invention and Trost which render the invention not anticipated.

Trost does not disclose oxygen nucleophiles having the specific structure required by the claims. That is, ". . . wherein the oxygen nucleophilic agent. . . is a compound containing

an oxygen atom expressed by AO-H or its deprotonated form AO⁻ . . ." Trost neither discloses nor suggests such a specific structure.

While the Examiner asserts that Trost discloses that oxygen nucleophiles may be used, Trost discloses nothing more than a general description "the carbon nucleophiles can be replaced with oxygen or nitrogen nucleophiles". Thus, Trost does not disclose with specificity the oxygen nucleophiles having the specific structure defined in the present claims and cannot anticipate the present claims which require this structure.

Furthermore, Trost does not exemplify the invention, nor does it teach the invention with sufficient specificity to amount to anticipation. To anticipate an invention, the prior art must disclose the invention with sufficient specificity or permit one to immediately envisage it, see MPEP 2131.02(A).

Reference patent's generic formula encompasses a vast number and perhaps even an infinite number of compounds; even though applicants' claimed compounds are encompassed by this broad generic disclosure, disclosure by itself does not describe applicants' claimed invention within meaning of 35 U.S.C. 102(b). *In re Petering and Fall*, 133 USPQ 275; 301 F2d 676 (CCPA 1962)

"[E]arlier disclosure of a genus does not necessarily prevent patenting a species member of that genus," *Eli Lilly & Co. v. Bd of Regents of the Univ. of Washington*, 334 F.3d 1264, 1270 [67 USPQ2d 1161] (citing *Bristol-Myers Squibb Co. v. Ben Venue Labs., Inc.*, 246 F.3d 1368, 1380 [58 USPQ2d 1508] (Fed. Cir. 2001)).

Here, Trost discloses a broad genus of catalysts ("any trivalent phosphorous compound", col. 3, lines 43-44). Like the situation in *Petering*, this represents a vast number and potentially unlimited number of compounds. On the other hand, the invention is directed to a monodentate phosphate having formula (I). Moreover, Trost discloses a process which uses a vast, potentially unlimited number, of different carbon or oxygen nucleophiles, while the invention is directed to oxygen nucleophiles expressed by the formula AO-H or AO⁻. On

both accounts, Trost does not permit one to immediately envisage the claimed process and cannot anticipate the invention.

As noted above, Trost discloses nothing more than the general description "The carbon nucleophiles can be replaced with oxygen or nitrogen nucleophiles". Trost indicates that any one of a phosphorus compound, a phosphine or a phosphite may be used as well as that carbon nucleophiles and oxygen nucleophiles may be used equally. Trost does not disclose any specific combination of a phosphite and an oxygen nucleophilic agent. It discloses only a combination of a phosphine and a carbon nucleophilic agent in its Examples. Accordingly, this rejection should be withdrawn since Trost does not disclose the structure of the oxygen nucleophilic agent required by the invention, nor does it exemplify the invention, nor does it teach the combination of a phosphate and an oxygen nucleophilic agent with sufficient specificity to anticipate the invention.

While Trost has not been applied under 35 U.S.C. §103, to expedite prosecution, the Applicants now explain why Trost does not render the invention obvious.

(i) A characteristic feature of the invention resides in that in its ability to produce a desired second allyl compound using an oxygen nucleophilic agent having a specific structure. As recognized by the inventors, an excellent characteristic activity can be developed by combining the required oxygen nucleophilic agent with a specific phosphite compound.

The problems solved by selecting a specific oxygen nucleophilic agent as well as a particular type of phosphate compound are clearly disclosed on page 5, lines 14 to 25 of the specification. Trost does not disclose or suggest that such a remarkable effect can be developed by combination of these compounds.

It has been an on-going goal or objective to those of skill in the art to improve the activity and selectivity of reactions. However, it requires significant research and discoveries

to do this, since the activity and selectivity of such reactions can fundamentally change depending on the type of phosphorous ligand used. Namely, even if it is known that some specific phosphorus ligand is capable of efficiently effectuating some reaction, it is difficult to predict that some other ligand would also do so. Variation in steric and electronic properties of phosphorous ligands make it difficult to predict the reactivity of phosphorous ligands.

(ii) On the other hand, many methods have been proposed to parameterize and categorize the characters of different phosphorous ligands. Among them, the parameters of phosphorus ligand of Tolman are well known to those skilled in the art--see Tolman, Chemical Reviews, 1977, Vol. 77, No. 3, pages 313-348 (attached).

Tolman discloses that as parameters for classifying phosphorus ligands, Θ and v as parameters for steric effect and electronic effect, respectively, are very useful. Namely, ligands showing similar values in both of Θ and v show similar reactivities. Further, if the Θ and v parameters of two ligands are different, these ligands would show different reactivities.

For example, even if some phosphorus ligand having a large steric hindrance (i.e., where Θ is large) and a large electron donative property (where v is small) is suitable for some reaction, some other reaction may require as a suitable ligand a phosphorous ligand having a large steric hindrance (Θ is large) and small electron donative property (v is large). Further, in such a reaction, it cannot be said that the larger the value Θ is, the better. In some cases, a phosphorous ligand having Θ within an optimum range is preferred.

Namely, the optimum combination of Θ and v values depends on the reactions, and it is difficult to predict that some phosphorous ligand with specific Θ and v values excellent for some reaction may suitably be used for other reactions.

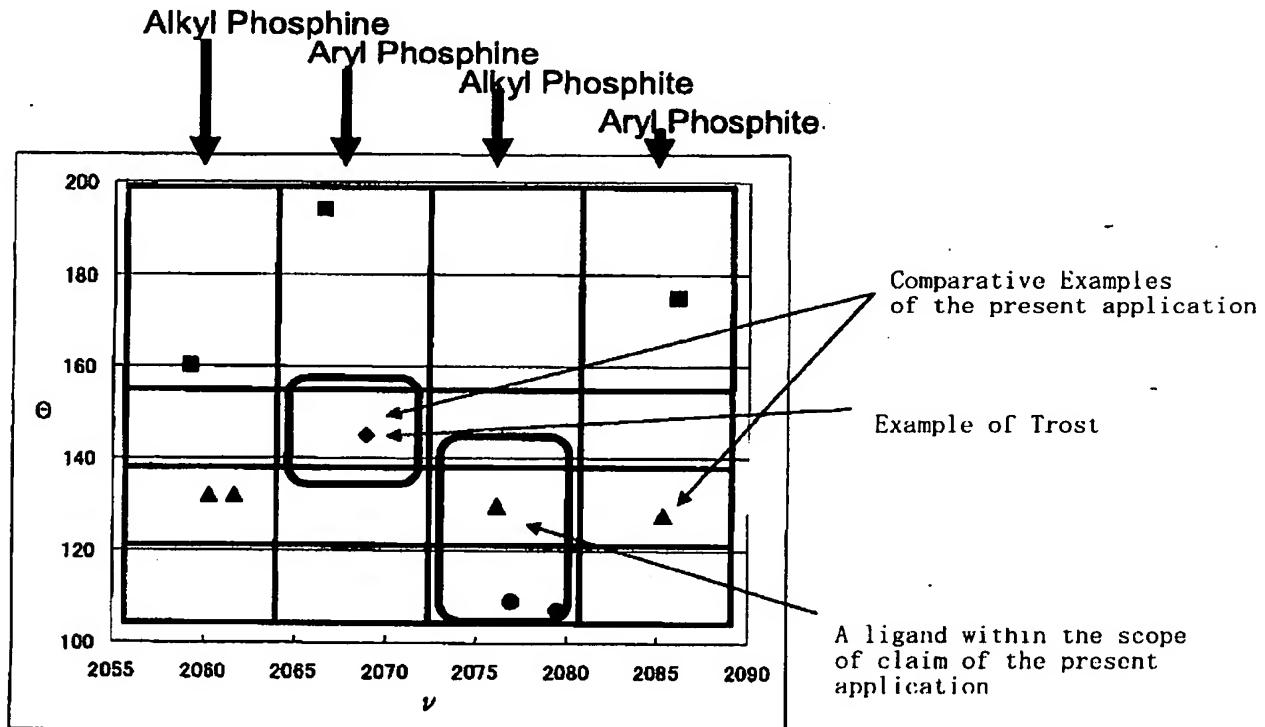
(iii) As depicted below, the steric and electron structures of phosphorous ligands described in Trost are different from the steric and electron structures of the phosphorous

ligand of the present invention. In the following Table 1, the Θ and ν values of the phosphorous ligand indicated in Appendixes A and B of Tolman are summarized.

Table 1

	ν	Θ
PiPr ₃	2059.2	160
Pbu ₃	2060.3	132
Pet ₃	2061.7	132
P(o-Tol) ₃	2066.6	194
PPh ₃	2068.9	145
P(OiPr) ₃	2076.1	130
P(OEt) ₃	2077	109
P(Ome) ₃	2079.5	107
P(OPh) ₃	2085.3	128
P(O-o-C ₆ H ₄ -t-Bu) ₃	2086.1	175

Further, in the following Fig. 1, the Θ and ν values of respective ligands are plotted. To simplify this explanation, the Θ and ν values are classified into four ranges (columns), respectively, and into 16 areas as shown in the following graph (Fig. 1):



(iv) The ν value indicates the electronic effect and shows that the larger the value is, the more electron donative the phosphorous ligand is. Further, the four ranges (columns) of the ν value in the above graph correspond to "alkylphosphine", "aryl phosphine", "alkyl phosphite" and "aryl phosphite" in order from small value to large value. The Θ value indicates the steric effect and shows that the smaller the value is, the smaller the steric hindrance of the phosphorous ligand is. This Θ value depends on the steric structure of a phosphorous substituent.

Trost describes that in addition to PPh_3 , alkyl phosphine and alkyl phosphite may be used, but does not exemplify such. As is apparent from the above graph, PPh_3 is an aryl phosphine having different reactivity parameters (e.g., belonging to area in the above graph) than the areas in which alkyl phosphine and alkyl phosphite fall. Namely, based on the

above, that the alkyl phosphine and alkyl phosphite would show a different reactivity from PPh_3 .

Further, the Trost ligand is effective for not only carbon nucleophiles but also oxygen nucleophiles. However, Trost describes only the reaction with carbon nucleophiles in the Examples. Namely, in Trost, based on the Example of the reaction with a carbon nucleophile using an aryl phosphine as a ligand, it is described that Trost's invention is effective for a different reaction using another phosphorous ligand (reaction with an oxygen nucleophile). However, as mentioned above, it is difficult to predict the reactivity of a different reaction using a phosphorous ligand having a parameter which belongs to different area, see Fig. 1 above.

(v) As exemplified in the specification, when PPh_3 as an aryl phosphine (Comparative Example 5) and $\text{P}(\text{OPh})_3$ (Comparative Example 6) as an aryl phosphite are used, the reaction with an oxygen nucleophilic agent does not efficiently proceed. On the other hand, when $\text{P}(\text{O}i\text{Pr})_3$ (Example 3) as an alkyl phosphite which falls within the scope of claim of the present invention is used, excellent reactivity is seen. Accordingly, the inventors have found an optimum area for the reaction with an oxygen nucleophilic agent which is not disclosed or suggested by the prior art. This discovery clearly represents an inventive step (is indicative of non-obviousness) of the claimed invention.

	Ligand	Oxygen nucleophilic agent	Yield of the second allyl compound
Example 3	Triisopropyl phosphite	1-Octanol	38%
Comparative Example 5	Triphenyl phosphine	1-Octanol	7%
Comparative Example 6	Triphenyl phosphite	1-Octanol	3%

As is evident from the above Table, the yield of the desired second allyl compound is very low when an oxygen nucleophilic agent and a phosphine compound are combined. Even when an oxygen nucleophilic agent is combined with a phosphite compound unlike

those required by the invention (a triphenyl phosphate that does not have the required straight or branched alkyl group, e.g., triphenyl phosphite), the yield of the secondary allyl compound is very low (e.g. 3% for triphenyl phosphate).

As mentioned above, Trost neither discloses nor suggests that the catalyst having a high activity can be obtained by selecting an oxygen nucleophilic agent having a specific structure and a phosphite compound having a specific structure.

(vi) Claim 7 is novel and unobvious for the reasons above, thus, Claims 8-16, 18-26 and 30-32 are also novel and unobvious.

In view of the remarks above, the Applicants respectfully request that the rejection based on Trost be withdrawn.

Rejection—35 U.S.C. §103

Claims 7-16, 18-26 and 30-32 were rejected under 35 U.S.C. 103(a) as being unpatentable over Kurtz et al., U.S. Patent No. 3,755,451, in view of Bryant, U.S. Patent No. 3,534,088 or Hefner, Jr., U.S. Patent No. 4,613,703. The prior art does not suggest or provide a reasonable expectation of success for the invention for the reasons previously discussed, none of which suggests or provide a reasonable expectation of success for the present method involving selected oxygen nucleophilic agents and selected phosphate catalysts.

Commensurate in Scope. The Official Action asserts that the showing in Tables 1 and 2 of the specification are not commensurate in scope with the protection sought, but does not provide a technical rationale for this assertion. Moreover, it is unclear whether this statement is directed to the independent claim, or whether it applies to the dependent claims as well. As discussed above, a characteristic feature of the present invention resides in that an oxygen nucleophilic agent having a specific structure and a phosphite compound having a specific

structure are selected. The prior art does not suggest selection of such compounds, nor does it provide a reasonable expectation of success for the superior properties of a process selecting these particular types of compounds.

The phosphite compound of the specific structure means that phosphate compounds having aromatic substituents, such as triphenyl phosphate, are not selected. Tables 1 and 2 show the effects of selecting phosphites having linear or branched alkyl groups as opposed to other substituents such as phenyl and thus support the scope of the present claims, which are directed to phosphites having linear or branched alkyl substituents.

(ii) As explained above with reference to Tolman, even if a longer alkyl group substituent in the phosphorous ligand is used, the parameter of the ligand will not be substantially changed. For example, in comparison between PEt₃ and PBu₃, the ν values are 2061.7 and 2060.3, respectively, and the Θ values are 132 in both cases. Further, in comparison between P(OMe)₃ and P(OEt)₃, the ν values are 2079.5 and 2077.0, respectively, and the Θ values are 107 and 109, respectively. Thus, even if the length of the alkyl group substituent in the phosphorous ligand were extended, these values would remain within the same area as shown by the Fig. 1 above. Thus, other alkyl substituents for the R groups in formula (1) of Claim 7, would be expected to provide phosphites with similar functional properties.

Based on the above, including the exemplified reactions involving P(OEt)₃ and P(OiPr)₃, one with ordinary skill in the art would not any reason to doubt that phosphites having longer alkyl chains, such as P(OBu)₃, P(OOctyl)₃ and P(OsBu)₃, would not effectively function in the claimed method. Thus, while the Examiner alleges these results are not commensurate in scope, no technical rationale for this assertion, and *a fortiori* ("for an even stronger reason") no rationale rebutting the above technical remarks has been presented.

Accordingly, the Applicants respectfully request that this rejection be withdrawn.

Conclusion

After consideration of the remarks above, the Applicants respectfully request withdrawal of the rejections of record and allowance of this application.

Respectfully submitted,

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Steric Effects of Phosphorus Ligands in Organometallic Chemistry and Homogeneous Catalysis[†]

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I. Introduction

It has long been recognized that changing substituents on phosphorus ligands can cause marked changes in the behavior of the free ligands and of their transition metal complexes. Prior to 1970, nearly everything was rationalized in terms of electronic effects, although there were scattered references to steric effects. In that year, quantitative measures of electronic¹ and steric² effects were proposed—based on A_1 carbonyl stretching frequencies (ν) in $\text{Ni}(\text{CO})_3\text{L}$ complexes, and ligand cone angles (Θ) of space-filling CPK molecular models.³ Since then a large

[†] In honor of Professor Richard C. Lord on the occasion of his 65th birthday.

number of papers have appeared which show that steric effects are generally at least as important as electronic effects and can dominate in many cases. Molecular structures, rate and equilibrium constants, NMR chemical shifts, and even relative infrared intensities have been correlated with ligand cone angles.

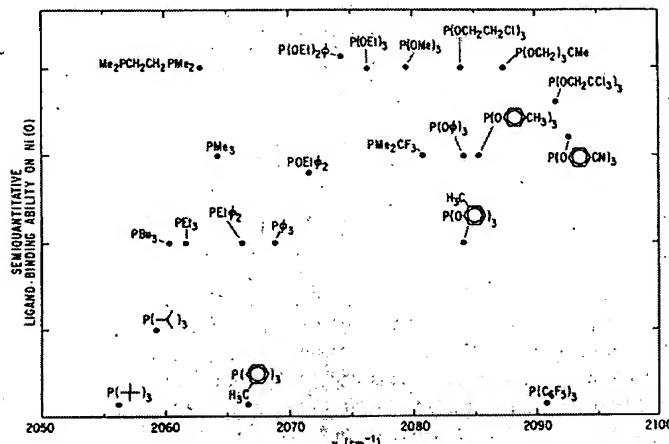
There have been no reviews of phosphorus ligand steric effects, though Pidcock⁴ did devote a short section to the subject in his chapter in "Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands", published in 1973. For background reading on steric effects in organic chemistry, the reader should see books by Brown⁵ and Taft.⁶ I have not attempted a comprehensive coverage of the literature but rather have selected works, published through 1975, which best illustrate the basic principles. Though phosphorus ligands are of primary interest, I have included some data on ligands coordinated by As, Sb, and Bi. For the convenience of the reader, values of ν and Θ are tabulated in Appendixes A and B. For purposes of comparison, Appendix C gives cone angles for a few ligands of other types, such as H, halogen, alkyl, acyl, CO, and $\pi\text{-C}_5\text{H}_5$.

Abbreviations used include:

Me	methyl
Et	ethyl
Pr	propyl
Bu	butyl
Ph	phenyl ($\phi = \text{Ph}$ in figures)
Ar	aryl
Bz	benzyl
Cy	cyclohexyl
Np	naphthyl
Cp	cyclpentadienyl
Pz	pyrazolyl
Tol	tolyl
L	any monodentate phosphorus ligand
dmpe	$\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$
P_3	$\text{CH}_2\text{C}(\text{CH}_2\text{PPh}_2)_3$
X	an anionic ligand, generally a halogen
DH	dimethylglyoximato
TPP	tetrphenylporphyrin
salen	N,N' -ethylenebis(salicylideneiminato)
$\mu\text{-CO}$	a bridging carbonyl
acacen	N,N' -ethylenebis(acetylacetoniminato) (see 41)
diop	2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (see 92)
ν	$\nu_{\text{CO(A}_1\text{)}}$ of $\text{Ni}(\text{CO})_3\text{L}$ in CH_2Cl_2 in cm^{-1}
Θ	the ligand cone angle in degrees
δ	an NMR chemical shift
Δ	coordination chemical shift ($\delta_{\text{complex}} - \delta_{\text{free}}$)
μ	an electric dipole moment
$E_{1/2}$	a half-wave potential in electron volts
D	Debyes
BM	Bohr magnetons
S	any substituent on phosphorus



Figure 1. A schematic definition of electronic and steric effects.

Figure 2. The semiquantitative ability of various ligands to compete for coordination on Ni(0) plotted against ν , from ref 2.

Phosphorus ligands with different substituents are generally written with the substituents given in order of increasing size, for example, PHMe₂, PMe₂Ph, or PPh(*t*-Bu)₂.

A. Definition of Electronic and Steric Effects

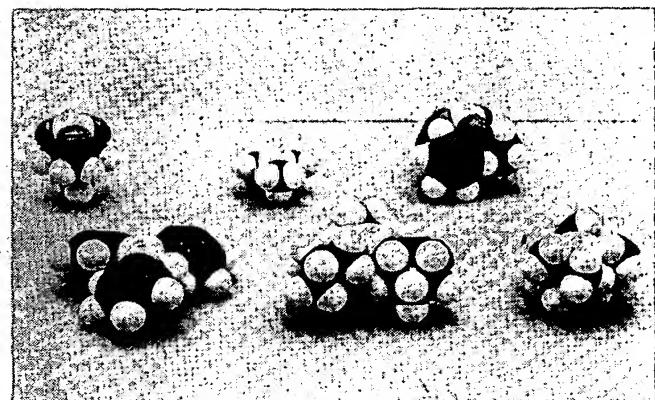
By *effect* I mean: changes in molecular properties as a result of changing part of a molecule
electronic—as a result of transmission along chemical bonds, for example, changing from P(*p*-C₆H₄OCH₃)₃ to P(*p*-C₆H₄Cl)₃
steric—as a result of forces (usually nonbonding) between parts of a molecule, for example, changing from P(*p*-C₆H₄CH₃)₃ to P(*o*-C₆H₄CH₃)₃. Special cases involve bonding between parts of a molecule, as in going from P(OEt)₃ to P(OCH₂)₃CMe or on changing *n* in a chelate complex, [Ph₂P(CH₂)_nPPh₂]M.

A nonverbal definition is shown in Figure 1.

It is important to realize that steric effects can have important electronic consequences and vice versa. For example, increasing the angles between substituents will decrease the percentage of s character in the phosphorus lone pair. Changing the electronegativity of atoms can also affect bond distances and angles.⁷ Thus, electronic and steric effects are intimately related and difficult to separate in any pure way. A practical and useful separation can be made, however, through the parameters ν and Θ .

B. The Electronic Parameter ν

Strohmeier⁸ showed that phosphorus ligands can be ranked in an electronic series (based on CO stretching frequencies) which is generally valid for a wide variety of monosubstituted transition metal carbonyls. For our electronic parameter ν , we choose the frequency of the A₁ carbonyl mode of Ni(CO)₃L in CH₂Cl₂. We could have chosen some other carbonyl complex, but Ni(CO)₃L forms rapidly on mixing Ni(CO)₄ and L in a 1:1 ratio at room temperature, even if L is very large; the A₁ band is sharp and readily measurable with an accuracy of ± 0.3 cm⁻¹.

Figure 3. CPK molecular models of P(OCH₂)₃CMe, PMe₃, P(OPh)₃, PPh₃, and P(*t*-Bu)₃.TABLE I. Selected Values of ν (cm⁻¹)

L	ν	$\Delta\nu$
P(<i>p</i> -Tol) ₃	2066.7	0.1
P(<i>o</i> -Tol) ₃	2066.6	
PMe ₃	2064.1	2.4
PEt ₃	2061.7	2.5
P(<i>i</i> -Pr) ₃	2059.2	3.1
P(<i>t</i> -Bu) ₃	2056.1	

Frequencies for a large number of ligands are given in Appendix A. The additivity of substituent contributions χ_i (also given in Appendix A) shown in eq 1 makes it possible to estimate ν for a variety of ligands for which it has not been measured.¹

$$\text{For } \text{PX}_1\text{X}_2\text{X}_3 \quad \nu = 2056.1 + \sum_{i=1}^3 \chi_i \quad (1)$$

That ν is indeed a measure of electronic effects—not affected by crowding of the Ni(CO)₃ by the substituents on phosphorus—is suggested by the near identity of values for P(*p*-Tol)₃ and P(*o*-Tol)₃ in Table I and by the small and regular decreases in ν on replacing H by Me. [The decreasing electronegativity of the alkyl phosphines going down the series is, however, partly due to alkyl-alkyl repulsions, as we shall see in section III.F.]

C. The Steric Parameter Θ

The ligand cone angle Θ was introduced after it became clear that the ability of phosphorus ligands to compete for coordination positions on Ni(0) could not be explained in terms of their electronic character (Figure 2).² The ligands P(OCH₂)₃CMe, PMe₃, P(OPh)₃, PPh₃, PCy₃, and P(*t*-Bu)₃ show a decreasing binding ability in that order. CPK molecular models of these ligands (Figure 3) clearly show an increase in congestion around the bonding face of the P atom in the same order. The steric parameter Θ for symmetric ligands (all three substituents the same) is the apex angle of a cylindrical cone, centered 2.28 Å (2.57 cm) from the center of the P atom, which just touches the van der Waals radii of the outermost atoms of the model (see Figure 4). If there are internal degrees of freedom (e.g., rotation about P-C bonds), the substituents are folded back, as shown in Figure 3, to give a minimum cone. For values of Θ over 180°, measurements may be made more conveniently by trigonometry, as shown in Figure 5. Figure 6 indicates how an effective cone angle can be defined⁹ for an unsymmetrical ligand $\text{PX}_1\text{X}_2\text{X}_3$, by using a model to minimize the sum of half-angles shown in eq 2.

$$\Theta = (2/3) \sum_{i=1}^3 \theta_i/2 \quad (2)$$

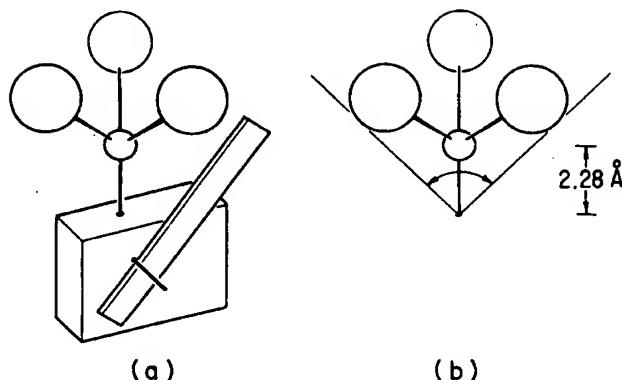


Figure 4. (a) Ligand angle measuring device; (b) the cone angle, from ref 2.

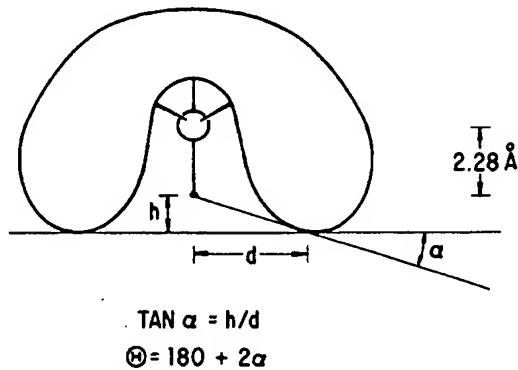
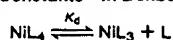


Figure 5. Method of measuring cone angles larger than 180°.

TABLE II. Equilibrium Constants^a In Benzene at 25°:



L	K_d , M	Original Θ, ^b deg	New Θ, deg
P(OEt) ₃	$<10^{-10}$ ^c	109	109
PM ₃	$<10^{-9}$ ^c	118	118
P(O-p-C ₆ H ₄ Cl) ₃	2×10^{-10}	~121	128
P(O-p-Tol) ₃	6×10^{-10}	~121	128
P(O-i-Pr) ₃	2.7×10^{-5}	114	130
PEt ₃	1.2×10^{-2}	132	132
P(O-o-Tol) ₃	4.0×10^{-2}	~165	141
PM ₂ Ph ₂	5.0×10^{-2}	^d	136
PPh ₃	^e	145	145

^a Selected values from ref 9. ^b From ref 2. ^c At +70 °C. ^d Θ for unsymmetrical ligands was not defined in ref 2. ^e No Ni(PPh₃)₄ was detected in solution: ref 58.

In the case of chelating diphosphines, $\theta_1/2$ can be taken as the angle between one M-P bond and the bisector of the PMP angle.⁹

A much better correlation of binding ability of ligands on Ni(0) with Θ is shown in Figure 7. [The values of Θ used (Appendix B) are not in all cases those reported originally.]

There is an approximate group additivity relationship for cone angles of unsymmetrical $\text{PX}_1\text{X}_2\text{X}_3$ ligands, which assumes that $\theta_1/2$ will be the same as in PX_3 . Physically this means that the orientation of substituent X_1 which minimizes Θ in eq 2 will be the same which minimizes Θ of PX_3 . Mathematically, Θ for PM₂Ph₂ is two-thirds of the way between PM₃ (118°) and PPh₃ (145°) or 136°.

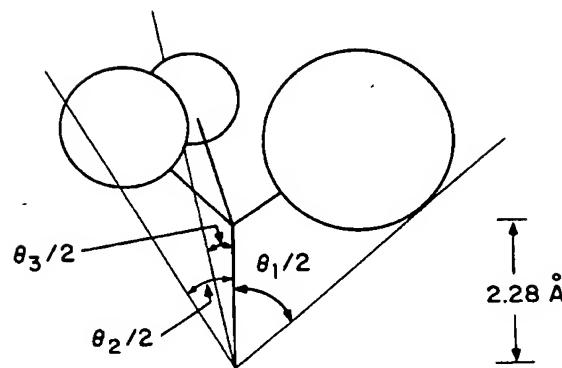


Figure 6. Method of measuring cone angles for unsymmetrical ligands.

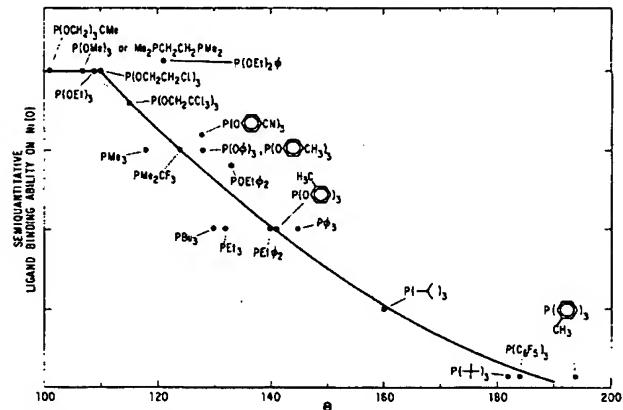


Figure 7. The data from Figure 2 plotted against Θ from Appendix B.

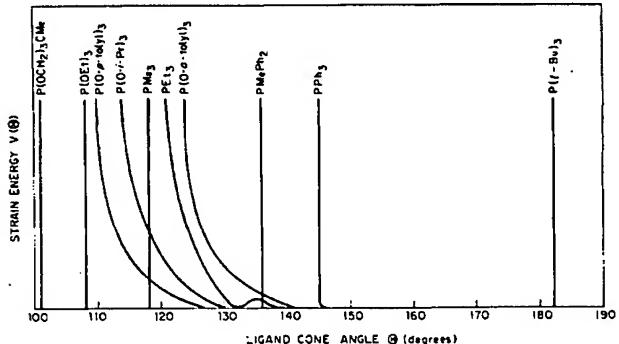


Figure 8. Strain energy in phosphorus ligand models as the ligand cone is compressed, from ref 9.

D. Limitations of the Molecular Models

For ligand models with fixed geometries [such as PF_3 , $\text{P}(\text{OCH}_2)_3\text{CMe}$, or $\text{P}(t\text{-Bu})_3$], or with only a few internal degrees of freedom (PM₃ or PPh₃), Θ can be rapidly and confidently measured to $\pm 2^\circ$. With more complex ligands, it may be difficult to decide when a minimum cone has been reached. It may be possible, as shown in Figure 8, to get still smaller angles by introducing strain (indicated by nonparallel faces between atoms). The question arises: How much strain in a model is realistic in terms of the behavior of real molecules? To answer, we must turn to chemical experiments.

NiL₄ dissociation equilibrium constants (Table II) show that K_d is not sensitive to changing para substituents in aryl phos-

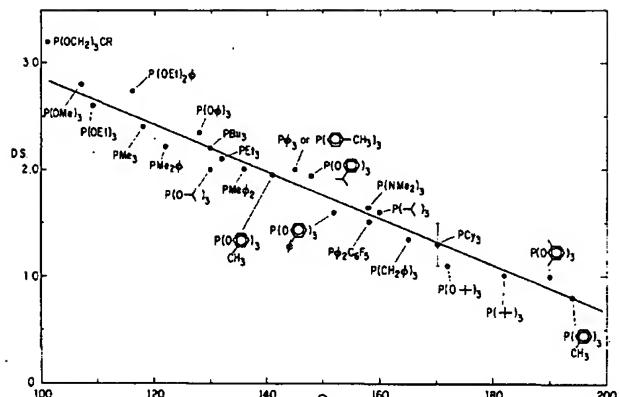


Figure 9. The degree of substitution (DS) of carbonyl groups from $\text{Ni}(\text{CO})_4$, as described in ref 2 and 10.

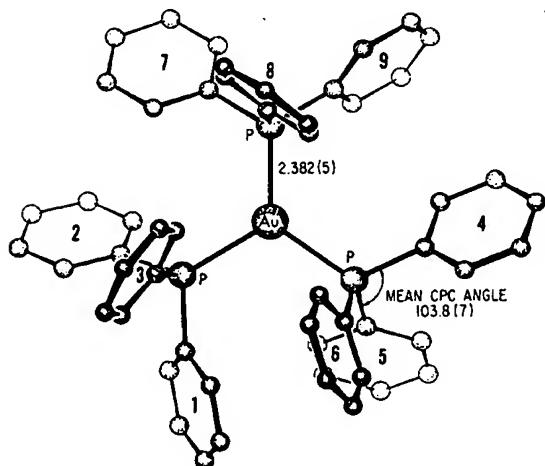


Figure 10. Structure of $\text{Au}(\text{PPh}_3)_3^+$, from ref 11.

phites. If we assume that steric effects dominate, the original values of Θ are clearly not in the right order for the experimental K_d : $\text{PPh}_3 > \text{P}(\text{O}-o\text{-Tol})_3$ and $\text{P}(\text{O}-i\text{-Pr})_3 > \text{P}(\text{O}-p\text{-Tol})_3$. Closer inspection of the models shows that 114° for $\text{P}(\text{O}-i\text{-Pr})_3$ requires a great deal of strain; an unstrained value is near 130° . The 165° for $\text{P}(\text{O}-o\text{-Tol})_3$ was measured² with all three methyl groups pointing toward P; pointing them away gives an essentially strain-free model at 141° . The similarity of K_d 's for PMePh_2 and $\text{P}(\text{O}-o\text{-Tol})_3$ and the fact K_d is larger for $\text{P}(\text{O}-p\text{-Tol})_3$ than for PMe_3 suggest that strain-free models give a more realistic picture of the size of real ligands.

In cases where Θ is difficult to measure with models, a value can be estimated from a simple experiment in which $\text{Ni}(\text{CO})_4$ is heated with an eightfold excess of L in a sealed tube.¹⁰ The degree of substitution (DS) of CO by L can be readily estimated from the IR spectrum in the carbonyl region.² Figure 9 shows the rather good correlation of DS with Θ , larger ligands replacing fewer CO's. The value of 1.25 for PCy_3 is the average of three determinations, with the average deviation indicated by error bars. On this basis, PCy_3 can be assigned a cone angle of 170° , rather than the original model-based value² of $179 \pm 10^\circ$. Several other types of experiments to be described also show that PCy_3 is significantly smaller than $\text{P}(t\text{-Bu})_3$, which has an accurately measurable $\Theta = 182^\circ$. It is such revised values of Θ which appear in Appendix B.

One difficulty with the ligand cone idea is that even symmetric real ligands do not have cylindrical symmetry. They can mesh into one another and achieve higher coordination numbers than

TABLE III. SPS Angles^a

L			
PH ₃			
93.8			
PF ₃	Ni(PF ₃) ₄	H ₃ B·PF ₃	OPF ₃
96.3	98.4	100	101.3
P(<i>o</i> -C ₆ H ₄) ₃ P			OP(<i>o</i> -C ₆ H ₄) ₃ PO
97.0 ^b			100.5 ^b
PM ₃			OPM ₃
98.9			~106
P(OCH ₂) ₃ CH ₂ Br			OP(OCH ₂) ₃ CMe
100.1 ^c			103.7 ^d
PCl ₃			OPCl ₃
100			103.8
PPh ₃	Au(PPh ₃) ₃ ⁺		OPPh ₃
103	103.8°		107
P(<i>t</i> -Bu) ₃	NiP(<i>t</i> -Bu) ₃ Br ₃ ⁻		

^a From ref 12 unless noted otherwise. ^b D. Schomburg and W. S. Sheldrick, *Acta Crystallogr., Sect. B*, **31**, 2427 (1975). ^c D. S. Milbrath, J. P. Springer, J. C. Clardy, and J. G. Verkade, *J. Am. Chem. Soc.*, **98**, 5493 (1976). ^d D. M. Nimrod, D. R. Fitzwater, and J. G. Verkade, *ibid.*, **90**, 2780 (1968). ^e Reference 11. ^f Estimated from ³¹IP NMR data in ref 53. ^g Reference 24.

might be expected. The meshing of three PPh_3 's ($\Theta = 145^\circ$) in a plane occurs in the structure¹¹ of $\text{Au}(\text{PPh}_3)_3^+$ (Figure 10); there are graphite-like interactions (about 3.4 Å spacings) between rings 1 and 6, 4 and 9, and 2 and 7.

Cone angles of the CPK models are based on a 2.28 Å M-P bond length and on tetrahedral angles about phosphorus. In real molecules both parameters are likely to vary. We have found, however, that variations in M-P or P-C bond lengths in the models of 0.1 Å seldom change Θ by more than 3 or 4°—not much more than the uncertainties in the measurements, and certainly not enough to cause gross distortions in the steric scale. Real M-P bond lengths vary from about 2.12 [Ni(PF₃)₄] to 2.55 Å [WCl₄(PMe₂Ph)₂] in a recent tabulation of structures;¹² 2.28 Å is about in the middle of the range. In any case, one is usually comparing complexes of one metal, where the metal covalent radius is fixed.

Angles between substituents on real phosphorus ligands are generally less than tetrahedral and can be changed by crowding, as we shall see in the next section, which describes steric effects on structures.

II. Structures of Real Ligands and Complexes

Angles between substituents on trivalent phosphorus (SPS angles) are invariably less than 109.5° , as seen in the first column of Table III, but approach tetrahedral as the substituents increase in size. Coordination to a transition metal, BH_3 , or O usually opens the angle by 3 or 4° .

This opening can be seen in the structure of $\text{P}(\text{CH}_2\text{O})_3\text{PFe}(\text{CO})_3\text{P}(\text{CH}_2\text{O})_3\text{P}^{13}$ in Figure 11. Notice that the carbonyl groups bend away from the larger PC_3 ligand ($\Theta = 114^\circ$, determined by the methylene hydrogens) toward the smaller PO_3 ($\Theta = 101^\circ$). The Fe-PO_3 bond is also shorter by 0.07 Å, but it is unclear to what extent the effect is steric or electronic. The same problem arises in the structures of $\text{Cr}(\text{CO})_5\text{PPPh}_3$ and $\text{Cr}(\text{CO})_5\text{P}(\text{OPh})_3$, where the Cr-P bond lengths differ by 0.11 Å (2.422 and 2.309 Å).¹⁴ In both Cr complexes, the four equatorial carbonyl groups are bent toward the axial CO to give average angles of about 88.5° .

The M-P bond is 0.075 Å shorter (2.406 vs. 2.481 Å) in *trans*-CpMo(CO)₂[P(OMe)₃]¹⁵ than in *trans*-CpMo(CO)₂[PPh₃]¹⁶. More electronegative substituents on P are expected to give a shorter M-P bond because they put more phosphorus's character into the bond. This is nicely shown by the 0.07-Å contraction (2.265 to 2.191 Å) in the Fe-P distance on going from

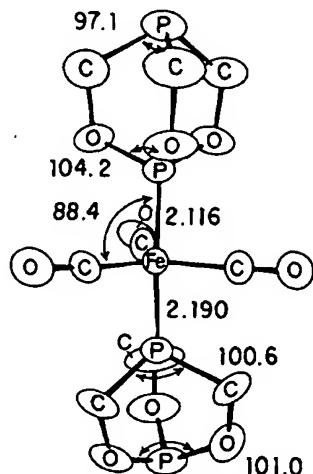
Figure 11. Structure of $\text{P}(\text{CH}_2\text{O})_3\text{PFe}(\text{CO})_3\text{P}(\text{CH}_2\text{O})_3\text{P}$, from ref 13.

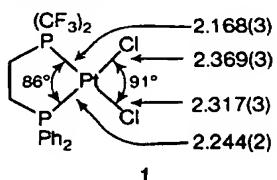
TABLE IV

Compound	$d(\text{Co-P})$, Å
$\text{CpNi}(\mu\text{-CO})_2\text{Co}(\text{CO})_2\text{PEt}_3$	2.238 (1) ^a
$\text{CpNi}(\mu\text{-CO})_2\text{Co}(\text{CO})_2\text{P}(\text{p-C}_6\text{H}_4\text{F})_3$	2.242 (3) ^b
$\pi\text{-MeC}_5\text{H}_4\text{Ni}(\mu\text{-CO})_2\text{Co}(\text{CO})_2\text{Ph}_2\text{Cy}$	2.269 (2) ^c

^a F. S. Stephens, *J. Chem. Soc., Dalton Trans.*, 1067 (1974). ^b I. L. C. Campbell and F. S. Stephens, *ibid.*, 340 (1975). ^c I. L. C. Campbell and F. S. Stephens, *ibid.*, 337 (1975).

$\text{CpFe}(\text{CO})_2\text{P}(\text{CF}_3)_2$ to its oxide $\text{CpFe}(\text{CO})_2\text{P}(\text{O})(\text{CF}_3)_2$.¹⁷ [The CPC angle opens from 94.5 (3) to 96.4 (3) $^\circ$.]

The substituents on the phosphorus atoms of 1¹⁸ are similar in size, but very different electronically. The Pt-P(CF_3)₂ bond is

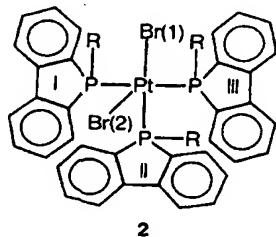


1

shorter by 0.07 Å and its trans Pt-Cl bond by 0.05 Å. These effects must be largely electronic. A very similar structure was found for the Pd analogue.¹⁹

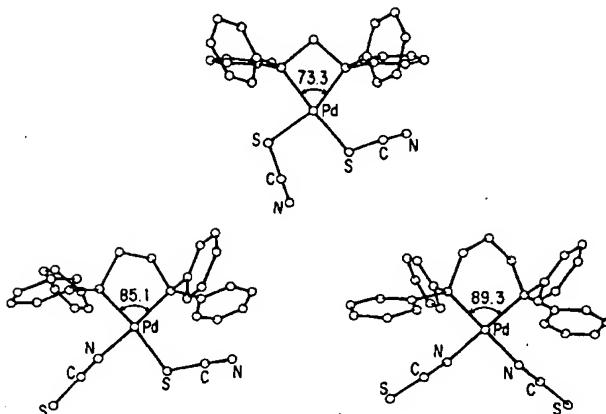
A role for steric effects is, however, evident in Table IV, where the Co-P bond lengths increase in the order of ligand size, not electron-acceptor character.

Data for a pair of electronically similar complexes 2 (R = Me or Et) are given in Table V. The more bulky ethyl ligand gives longer M-P bonds (as much as 0.03 Å) and longer M-Br (as much as 0.12 Å). The cis PMP and Br(2)MP angles increase by as much as 4 $^\circ$.



2

Table VI shows the effects of changing phosphorus substituents on the structures of some Cu(I) complexes. Going from

Figure 12. Structures of $[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]\text{Pd}(\text{SCN})_2$ complexes, from ref 20.TABLE V. Structural Data^a on Square-Pyramidal 5-Alkyl-5-H-dibenzophosphole Complexes (2)

	Bond Lengths, Å	
	R = Me	R = Et
M-P(I)	2.312 (5)	2.342 (5)
M-P(II)	2.248 (6)	2.257 (5)
M-P(III)	2.306 (6)	2.309 (5)
M-Br(1)	2.534 (3)	2.542 (3)
M-Br(2)	3.026 (3)	3.143 (3)

	Angles, Deg	
	P(I)MP(II)	P(I)MP(III)
P(I)MP(II)	98.40 (19)	98.55 (18)
P(I)MP(III)	168.57 (19)	166.87 (17)
P(II)MP(III)	92.62 (20)	93.01 (20)
Br(2)MP(I)	85.90 (14)	86.21 (13)
Br(2)MP(II)	108.34 (15)	
Br(2)MP(III)	88.09 (5)	

^a K. M. Chui and H. M. Powell, *J. Chem. Soc., Dalton Trans.*, 1879 (1974).

TABLE VI. Structural Data^a on Cu(I) Complexes

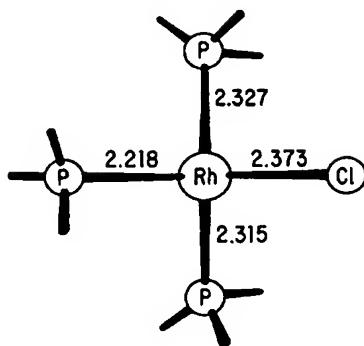
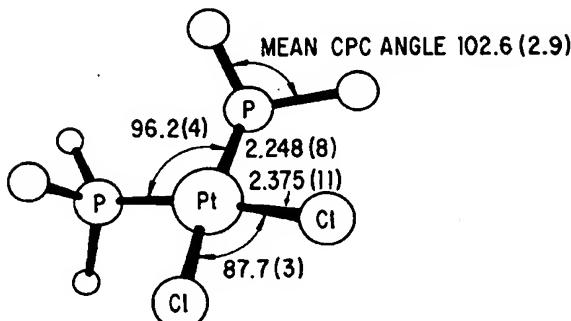
Complex	Dist Cu-P, Å	$\angle \text{PCuP}$, deg
$\text{Cu}(\text{NO}_3)_2(\text{PPh}_3)_2$	2.25	131.2 (1)
$\text{Cu}(\text{NO}_3)_2(\text{PCy}_3)_2$	2.29	140 (1)
$\text{Cu}(\text{B}_3\text{H}_8)(\text{PMePh}_2)_2$	2.25, 2.26	128 (1)
$\text{Cu}(\text{B}_3\text{H}_8)(\text{PPh}_3)_2$	2.27, 2.29	120.0 (1)

^a S. J. Lippard and G. J. Palenik, *Inorg. Chem.*, 10, 1322 (1971).

PPh_3 to PCy_3 in the nitrate complexes increases the Cu-P distance by 0.04 Å and the PCuP angle by 9 $^\circ$. Going from PMePh_2 to PPh_3 in the borane complexes increases the distances by only about 0.02 Å. In this case, the interaction with the borane is more important than between the phosphines, and the larger phosphine has a smaller PMP angle. (The PMePh_2 ligands have their smaller Me groups toward the B_3H_8 .)

Palenik and co-workers²⁰ have reported a nice example of steric effects on structure in the series $[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]\text{Pd}(\text{SCN})_2$ with $n = 1, 2$, or 3, shown in Figure 12. Not only does the PMP angle increase with increasing n , but the binding mode of the thiocyanates goes from N,N to N,S to S,S.

The 0.06-Å longer M-P distance in *trans*- $\text{PtI}_2(\text{PCy}_3)_2$ than in *trans*- $\text{PtBr}_2(\text{PEt}_3)_2$ (Table VII) has been attributed to greater steric crowding in the iodide complex. [The Pt-I distance is slightly longer (0.014 Å) than the value calculated from the Pt-Br distance and the difference in covalent radii of I and Br.] The shorter Pt-P distance in *trans*- $\text{H}_2\text{Pt}(\text{PCy}_3)_2$ approaches that in $\text{Pt}(\text{PCy}_3)_2$.

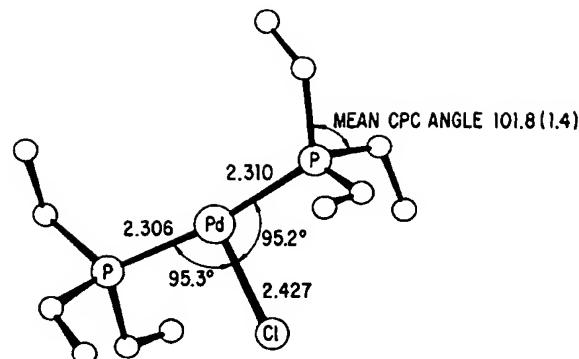
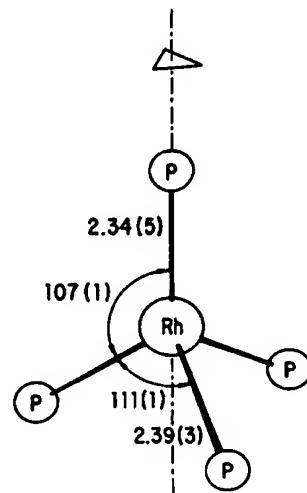
Figure 13. Structure of $\text{RhCl}(\text{PPh}_3)_3$, from ref 26.Figure 14. Structure of *cis*- $\text{PtCl}_2(\text{PMe}_3)_2$, from ref 28.TABLE VII. Pt-P Distances in *trans*- PtX_2L_2 Complexes

Complex	$d(\text{Pt-P}), \text{\AA}$	Ref
$\text{Pt}(\text{PCy}_3)_2$	2.231 (4)	23
$\text{H}_2\text{Pt}(\text{PCy}_3)_2$	2.25 (1)	22
$\text{PtBr}_2(\text{PEt}_3)_2$	2.315 (4)	21
$\text{PtI}_2(\text{PCy}_3)_2$	2.371 (2)	21

The unusually crowded molecule $\text{NiP}(\text{t-Bu})_3\text{Br}_3^-$ ²⁴ shows an exceptionally long Ni-P bond of 2.48 (1) Å, 0.20 Å longer than the more normal value of 2.28 Å in $\text{NiPPh}_3\text{I}_3^-$.²⁵ Average BrNiBr and INiI angles are 108.7 and 114.0°, respectively. The mean CPC angle of 107.0° in $\text{NiP}(\text{t-Bu})_3\text{Br}_3^-$ is one of the largest reported for a phosphine complex. An even larger value of 114.5° in $\text{HP}(\text{t-Bu})_3^+$ in the same crystal has been attributed²⁴ to the much smaller steric requirements of -H compared to -NI₃. This example does illustrate how the geometry within a phosphine can be significantly altered by contacts with other atoms in a complex. The P(t-Bu)₃ cone angle of $184 \pm 2^\circ$ in the anion, determined from the x-ray structure, is in good agreement with the 182° measured using CPK models.

There are many examples of structures where deviations from idealized geometries are attributable to steric effects. One example is the nonplanar arrangement of the heavy atoms in $\text{RhCl}(\text{PPh}_3)_3$ ²⁶ (Figure 13). The short Rh-P bond trans to Cl reflects a reduced trans influence of Cl relative to P (certainly an electronic effect), and results in a greater $^1J_{\text{RhP}}$ in the ^{31}P NMR spectrum.²⁷ The heavy atoms are also not coplanar in *cis*- $\text{PtCl}_2(\text{PMe}_3)_2$ ²⁸ (Figure 14). Steric crowding between the two phosphines is more severe than between the two halogens. The Pt-P length is 0.03 Å longer than in $\text{PtCl}_3(\text{PEt}_3)_-$,²⁹ where the deviations from an idealized square-planar geometry are much less (mean ClPtCl angle 89.4 (2)°).

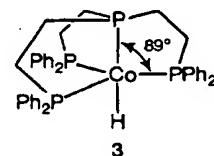
The crystal structure of $\text{Ir}(\text{PMePh}_2)_4^+$ shows a large tetrahedral distortion away from the idealized square plane.^{30a} Significantly, the compound does not react with O_2 or CO, although the closely

Figure 15. Structure of *trans*- $\text{HPdCl}(\text{PEt}_3)_2$, from ref 32.Figure 16. Structure of $\text{HRh}(\text{PPh}_3)_4$, from ref 33. The H presumably lies on the three-fold axis below the Rh.

analogous but less crowded $\text{Ir}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_4^+$ does, as does $\text{Ir}(\text{PMe}_2\text{Ph})_4^+$. The x-ray structure of both dioxygen complexes have been determined.^{30b}

It is common in hydride complexes to find distortions away from idealized geometries because of bending of ligands toward the less sterically demanding hydride.³¹ An example is *trans*- $\text{HPdCl}(\text{PEt}_3)_2$ ³² (Figure 15). The phosphines have rotated to minimize interaction of the methylene groups with the Cl. Going to *trans*- $\text{HPdCl}[\text{P}(\text{i-Pr})_3]_2$ increases the mean PMCl angle from 95.3 to 96.3°.³¹ With a smaller metal atom in *trans*- $\text{HNiCl}[\text{P}(\text{i-Pr})_3]_2$, the angle is still larger, 98.3°.³¹

The structure of $\text{HRh}(\text{PPh}_3)_4$ (Figure 16) has a threefold axis, but it is so far distorted from a trigonal bipyramidal that it is nearly tetrahedral.³³ In $\text{HRh}(\text{PF}_3)(\text{PPh}_3)_3$, where the smaller PF_3 is trans to H, the average angle between axial and equatorial phosphines is 99.3°.³⁴ Axial-equatorial phosphine angles of 89° are found in 3.^{35a}



The equatorial CO's in 4 are bent slightly toward the Mn-Mn bond (Table VIII) and staggered to reduce repulsive interactions. Phosphines of moderate bulk replace CO's in the less crowded

TABLE VIII. Structural Data for $Mn_2(CO)_{10}$ and Its Derivatives

	Mean angle MnMnC, deg	Dist Mn-Mn, Å	Dist MnP, Å
$(CO)_5Mn-Mn(CO)_5$ ^a	86.2 ± 1.4	2.92	
$(CO)_5Mn-Mn(CO)_4PMc_2Ph$ ^b	87.5	2.90	2.24
$PMc_2Ph_2(CO)_4Mn-Mn(CO)_4P-$ MePh ₂ ^c	86	2.90	2.23
$PEt_3(CO)_4Mn-Mn(CO)_4PEt_3$ ^d	87.6 ± 2.6	2.91	2.25

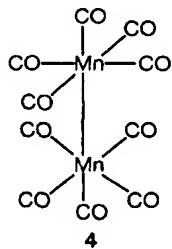
^a L. F. Dahl and R. E. Rundle, *Acta Crystallogr.*, **16**, 419 (1963). ^b M. Laing, E. Singleton, and R. Reimann, *J. Organomet. Chem.*, **58**, C21 (1973). ^c From ref 35b. ^d M. J. Bennett and R. Mason, *J. Chem. Soc. A*, 75 (1968).

TABLE IX. ^{31}P Chemical Shifts^a of Phosphines

Compound	$\angle SPS$, ^b deg	$\delta(^{31}P)$, ^c ppm	Θ , deg
PH ₃	93.8	+240 ^d	87
PMc ₃	98.9	+62	118
PEt ₃		+20.1	132
PPh ₃	103	+6.0	145
P(i-Pr) ₃		-20.0 ^e	160
P(t-Bu) ₃	105.7 ^f	-63.3	182

^a In ppm upfield of 85% H₃PO₄. ^b From ref 12. ^c From ref 53, unless noted otherwise. ^d From ref 37, p 238. ^e C. A. Tolman, unpublished result in THF. ^f Estimated from $^1J_{PC}$ in ref 53.

axial positions, but seem not to affect the structures much. AsMe₂Ph is sufficiently less sterically demanding than PMePh₂ that the disubstituted complex is diequatorial rather than diaxial.^{35b}



III. Spectroscopic Properties and Electron Distributions

A. NMR Chemical Shifts and Coupling Constants

1. ^{31}P Chemical Shifts

The electronegativity of substituents on phosphorus and the angles between them are the two most important variables determining ^{31}P chemical shifts and coupling constants.³⁶ The large range of phosphine chemical shifts in Table IX is striking, in view of the similar electronegativities of the substituents, but can be understood in terms of opening of SPS angles by steric crowding of the substituents. The cone angles (defined by the outermost edges of the ligands) also increase with the downfield shift of $\delta(^{31}P)$.

Grim's group contributions⁴¹ (GC_i) to ^{31}P chemical shifts of tertiary phosphines (Table X) can be similarly understood, though he first explained them in terms of hyperconjugation.

^{31}P shifts to high field can be anticipated if structural constraints require small CPC angles, as in 5 to 7. In 8, where the angles are constrained to 60°, the chemical shift is +450 ppm,⁴⁵ the highest $\delta(^{31}P)$ known.

Chemical shifts of acyclic alkyl phosphites (Table XI) are insensitive to changes in the bulk of the alkyl. The oxygens provide enough flexibility in the free phosphites that the OPO angles can

TABLE X. Grim's Group Contributions^a to $\delta(^{31}P)$

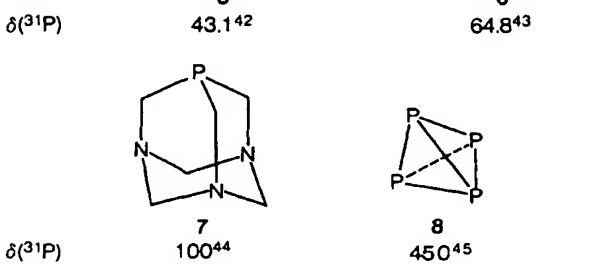
For $PR_1R_2R_3$	$\delta(^{31}P)_{calcd} = \sum_{i=1}^3 GC_i$
R _i	GC _i
Me	21
Neopentyl	18
i-Bu	15
Pr, Bu	11
Et	7
Bz	4
Ph	3

^a From ref 41.

TABLE XI. ^{31}P Chemical Shifts^a of Phosphites

Compound	$\angle OPO$, deg	$\delta(^{31}P)$, ^c ppm	Θ , deg
P(OCH ₂) ₃ CMe	100.1 ^b	-90.9 ^d	101
P(OMe) ₃		-139.7	107
P(OEt) ₃		-137.6	109
P(O-i-Pr) ₃		-137.5	130
P(O-i-Bu) ₃		-138.1 ^e	172

^a Negative values are ppm downfield from 85% H₃PO₄. ^b Angle for P(OCH₂)₃CCH₂Br from Table III. ^c From G. A. Olah and C. W. McFarland, *J. Org. Chem.*, **36**, 1374 (1971), except where noted otherwise. ^d From ref 2. ^e Neat liquid; C. A. Tolman, unpublished result.



remain essentially constant. The strained bicyclic phosphite, however, is ~50 ppm to higher field. Verkade⁴⁶ believes that this is not due to an unusually small OPO angle in the cage. Unfortunately, accurate OPO angles for the acyclic phosphites are not available.⁴⁷ A 50-ppm chemical shift difference for phosphites corresponds to a change in OPO angle of about 3°.⁴⁸

Gorenstein⁴⁹ has recently proposed an empirical correlation between ^{31}P chemical shifts of phosphates and OPO bond angles. The correlation is, however, not monotonic.

Coordination chemical shifts ($\Delta = \delta_{\text{complex}} - \delta_{\text{free}}$) depend on the nature of the metal and on the change in SPS angles on coordination.⁵⁰ Angle opening on coordination is consistent with the usually observed downfield shift (negative Δ). The magnitude of Δ tends to be less for larger ligands, as seen for *trans*-RhCl(CO)L₂ complexes in Figure 17. This is because SPS angles of ligands with large substituents generally open less on coordination.

In chelating diphosphine complexes, Δ depends on ring size (Table XII). Large downfield shifts are general for five-membered chelate rings.⁵¹ If a phosphorus is part of two or three five-membered rings as in 9 and 10, more negative values of Δ (in parentheses) can be found.⁵²

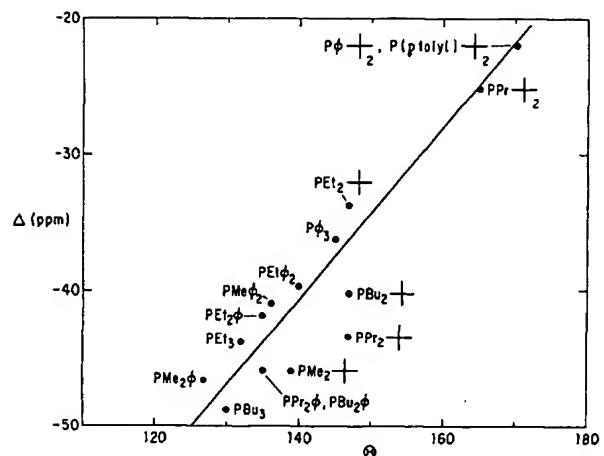


Figure 17. Correlation of change in ^{31}P chemical shift (ref 50) on coordination with Θ for $\text{RhCl}(\text{CO})\text{L}_2$ complexes.

TABLE XII. ^{31}P Data^a on $[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]\text{W}(\text{CO})_4$ Complexes

	$n = 1$	2	3
δ_{complex} , ppm	+23.6	-40.1	0.0
δ_{free} , ppm	+23.6	+12.5	+17.3
Δ , ppm	0.0	-52.6	-17.3
$^1J_{\text{WP}}$, Hz	202	231	222

^a S. O. Grim, W. L. Briggs, R. C. Barth, C. A. Tolman, and J. P. Jesson, *Inorg. Chem.*, **13**, 1095 (1974).

TABLE XIII. Coupling Constants in L and HL^+

Compound	$\angle \text{SPS}^a$	$^1J_{\text{PC}}$ in PR_3 , Hz ^b	$^1J_{\text{PH}}$ in HL^+ , Hz
$\text{P}(\text{OCH}_2)_3\text{CMe}$	100.1		898 ^c
$\text{P}(\text{OMe})_3$			827 ^d
$\text{P}(\text{O}-i\text{-Pr})_3$			796 ^d
$\text{P}(\text{o-C}_6\text{H}_4)_3\text{CH}$ (8)			571 ^e
PH_3	93.8		548 ^f
PMe_3	98.9	-13	505 ^f
PEt_3		+14	
PPh_3	103	+21 ^g	510 ^g
$\text{P}(i\text{-Bu})_3$		+19	455 ^g
$\text{P}(t\text{-Bu})_3$		+34	
PMe_4^+	109.5 ^h	+56	
PPh_4^+	109.5 ^h	+90 ^{g,i}	
$(\text{MeO})\text{PMe}_4$	120 ^j	+128 ^g	

^a From Table III unless noted otherwise. ^b From ref 53 unless noted otherwise. ^c L. J. Vande Griend and J. G. Verkade, *Phosphorus*, **3**, 13 (1973).

^d G. A. Olah and C. W. McFarland, *J. Org. Chem.*, **36**, 1374 (1971). ^e Reference 42. ^f Reference 40, p 18. ^g These values are anomalously high because of sp^2 C hybridization. ^h Tetrahedral by symmetry. ⁱ T. A. Albright, W. J. Freeman, and E. E. Schweizer, *J. Am. Chem. Soc.*, **97**, 2946 (1975).

^j For equatorial Me groups of the trigonal bipyramidal, from H. Schmidbaur, W. Buchner, and F. H. Köhler, *ibid.*, **96**, 6208 (1974).

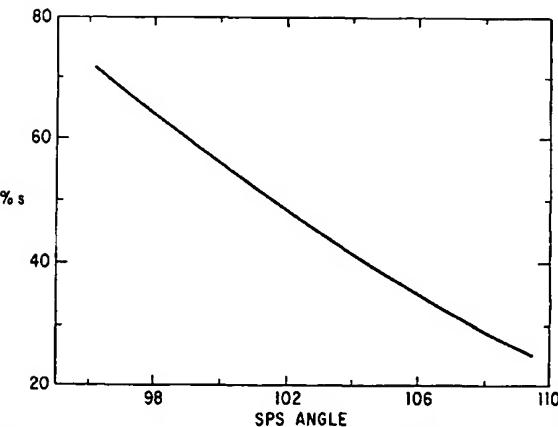
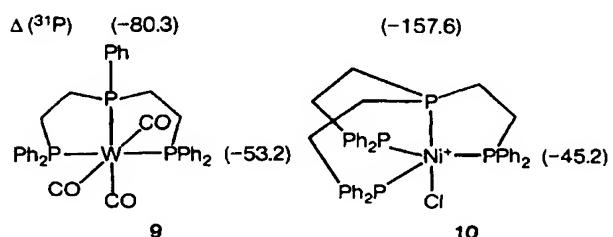


Figure 18. Dependence of the % s character of the phosphorus lone pair on the SPS angle, from ref 38, p 360.

TABLE XIV. P-P Coupling Constants^a in Diphosphines

Diphosphine	$^1J_{\text{PP}}$, Hz
Me_2PPMe_2	-180
$\text{Me}(i\text{-Bu})\text{PPMe}(i\text{-Bu})$	-290
$\text{Me}_2\text{PP}(i\text{-Bu})_2$	-318
$(i\text{-Bu})_2\text{PP}(i\text{-Bu})_2$	-451

^a H. C. E. McFarlane and W. McFarlane, *Chem. Commun.*, 582 (1975).

TABLE XV. ^{31}P NMR Data^a for $\text{SeP}(\text{C}_6\text{H}_4\text{X})_3$ and $\text{P}(\text{C}_6\text{H}_4\text{X})_3$

X	$^1J_{\text{PSe}}$, Hz	δ_{PSe}	δ_{P}
$p\text{-Cl}$	753	+2.2	+3.1
H	735	(0.0)	(0.0)
$m\text{-CH}_3$	726	-0.2	-0.2
$p\text{-CH}_3$	724	+1.6	+2.5
$p\text{-OCH}_3$	719	+3.8	+4.6
$o\text{-CH}_3$	708	+7.6	+24.6

^a From R. P. Pinnell, C. A. Megerle, S. L. Manatt, and P. A. Kroon, *J. Am. Chem. Soc.*, **95**, 977 (1973). Chemical shifts are in ppm upfield of the unsubstituted parent.

2. Coupling to ^{31}P

Opening of SPS angles increases the phosphorus s character in the P-S bonds and decreases it in the lone pair (see Figure 18). This is reflected in the coupling constants shown in Table XIII. Mann⁵³ used $^1J_{\text{PC}}$ in $\text{P}(i\text{-Bu})_3$ to estimate a CPC angle of 105.7°.

There are clearly also electronegativity effects in Table XIII. Because of the greater electronegativity of oxygen compared to carbon, protonated phosphites show a larger $^1J_{\text{PH}}$ than protonated phosphines with the same SPS angles.

Decreasing s character in the P-P bond of the diphosphines shown in Table XIV causes a marked lowering of $^1J_{\text{PP}}$ (more negative) as Me is replaced by *t*-Bu. The signs and magnitudes were determined by ^1H - ^{31}P double resonance techniques.

The P-Se coupling in Table XV shows both electronic and steric effects. More electronegative para substituents give higher coupling constants (more s character in the lone pair). The low value of $^1J_{\text{PSe}}$ for $\text{SeP}(o\text{-Tol})_3$ is presumably caused by CPC angle opening; however, the high-field shift of $\text{P}(o\text{-Tol})_3$ is unusual. (It may involve an interaction of the ortho methyl groups with the P lone pair, or a special feathering of the benzene rings.)

Metal-phosphorus coupling constants depend on both electronic and steric factors. Grim and co-workers⁵⁴ found that $^1J_{\text{WP}}$ in $\text{LW}(\text{CO})_5$ complexes is dominated by electronic effects,

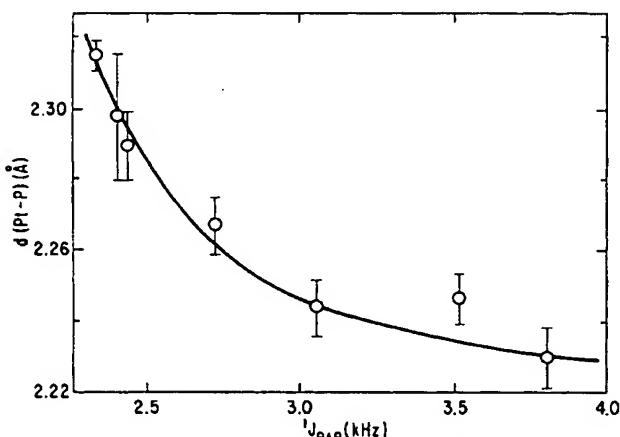


Figure 19. Correlation of $d(Pt-P)$ with $^1J_{PtP}$ in Pt(II) and Pt(IV) complexes of PEt_3 and PBu_3 , from ref 55.

judging from a good correlation of $^1J_{WP}$ with the frequency of the strongest ν_{CO} band (Table XVI). Steric effects in their study may be masked, however, by the large uncertainties in $^1J_{WP}$ and by the limited range of cone angles employed (130 – 157°).

Pidcock and co-workers⁵⁵ have shown a good inverse correlation (Figure 19) between $^1J_{PtP}$ and Pt-P bond lengths in PEt_3 and PBu_3 complexes of Pt(II) and Pt(IV). They suggest that the decreasing $^1J_{PtP}$ for PEt_3 trans to Cl in 11 to 13 may be due primarily to steric distortions.

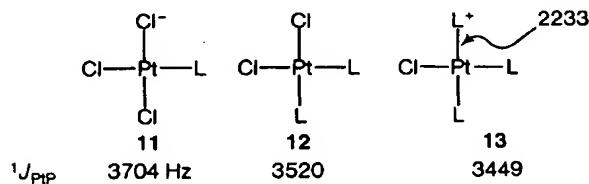
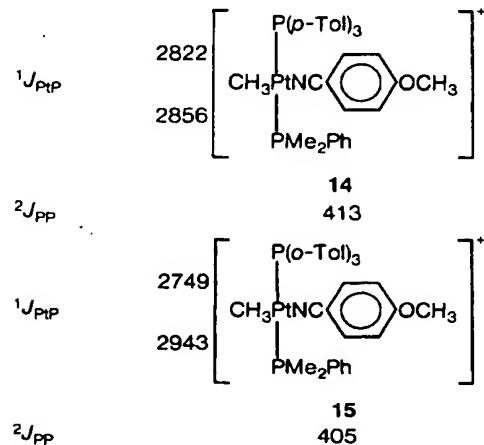


Table XVII shows substantially smaller $^1J_{PtP}$ for PEt_3 than for $PMes_3$ in the crowded PtX_4L_2 complexes. $^2J_{PP}$ is always ~ 70 Hz less for PEt_3 .

The coupling constants⁵⁶ in 14 and 15 show similar effects. Here the weakening of the upper Pt-P bond on going from $P(p\text{-Tol})_3$ to $P(o\text{-Tol})_3$ is reflected in a strengthening of the lower one. The changes in $^1J_{PtP}$ (from Figure 19) correspond to changes in bond length of 0.004 Å.



Values of $^2J_{PP}$ in $M(CO)_4L_2$ complexes have been correlated with the electronegativity of atoms attached to P.⁵⁷ However, the absolute values of $^2J_{PP}$ in *cis*- $M(CO)_4L_2$ complexes con-

TABLE XVI. NMR and IR Data^a for $LW(CO)_5$ Complexes

L	$^1J_{WP}$ (± 8 Hz)	Strongest ν_{CO} (± 1 cm^{-1})
PPh_3	280	1942
$PBuPh_2$	250	1938
$PMes_2$	245	1939
$PPh_2(i\text{-Bu}), PPh_2(i\text{-Pr}), PEtPh_2$	240	1937, 1937, 1938
PBu_2Ph	235	1937
PBu_3	200	1934

^a From ref 54. See also J. G. Verkade, *Coord. Chem. Rev.*, **9**, 1 (1972).

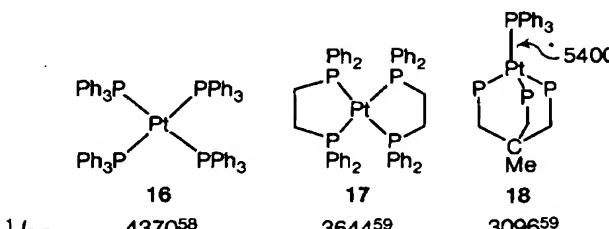
TABLE XVII. NMR Coupling Constants^a

Complex	X	$^1J_{PtP}$, Hz		$^2J_{PP}$, Hz	
		$PMes_3$	PEt_3	$PMes_3$	PEt_3
<i>trans</i> - PtX_4L_2	Cl	1516	1461	660	587
	Br	1550	1471	645	574
<i>trans</i> - PtX_2L_2	Cl	2379	2408	510	438
	Br	2336	2336	514	449

^a R. J. Goodfellow and B. F. Taylor, *J. Chem. Soc., Dalton Trans.*, 1876 (1974).

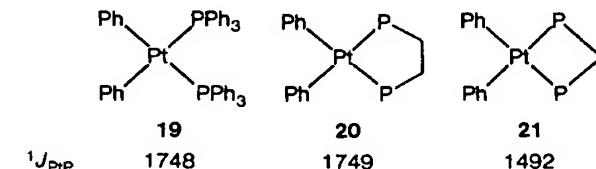
tralizing $P\text{-NR}_2$ groups were too small, tentatively attributed to opening of the PMP angles by steric interactions.

Metal-phosphorus coupling constants depend on structural constraints in chelates (see Table XII). A marked effect can be seen in comparing 16, 17, and 18. The $PPtP$ angles in the triphosphine of 18 are all restricted to $\sim 90^\circ$, tending to concent-



trate Pt's character in the fourth Pt-P bond. It is noteworthy that 18 is dissociatively stable up to 60°C whereas 16 is completely dissociated to $Pt(PPh_3)_3$ and PPh_3 at $+25^\circ\text{C}$.⁵⁸

The small value of $^1J_{PtP}$ ⁵⁹ in 21 is due to the small $PPtP$ angle of 73° .⁶⁰ The Pt-P bond lengths [2.30 (1) Å] are normal.



3. 1H Chemical Shifts and Coupling Constants

Perhaps the most surprising steric effect on 1H NMR chemical shifts is shown (Figure 20) by the methanol protons in the $[(CH_3OH)Co(DH_2)_2L]^+$ complexes of Troglar and Marzilli.⁶¹ Near independence of electronic effects is suggested by the similar shifts for $P(CH_2CH_2CN)_3$ and PBu_3 ($\delta = 2077.9$ and 2060.3 cm^{-1} , respectively). There seems to be little steric effect until Θ reaches $\sim 120^\circ$, presumably where the interaction with the planar dimethylglyoximato ligand becomes important. The authors have tried to fit their data with a model which assumes that the increased shielding for larger L arises from a distortion of the ring from planarity, but the calculated shifts are much smaller

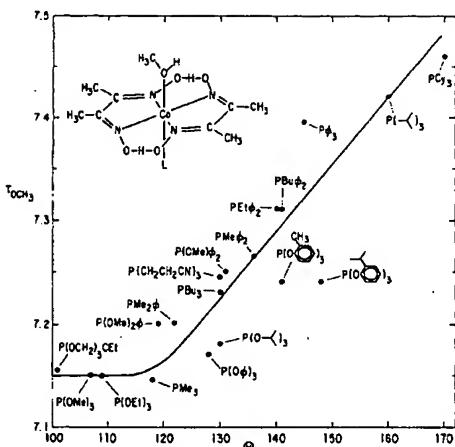


Figure 20. ^1H chemical shift of methanol CH_3 in $[(\text{CH}_3\text{OH})\text{Co}(\text{DH})_2\text{L}]^+$ complexes (ref 61) against θ .

TABLE XVIII. ^1H NMR Data^a for H_A and H_B in $\text{CpFe}(\text{CO})\text{LCH}_2\text{R}$

R	L	$\Delta\delta$, ppm	$^3J_{\text{PH}_A}$, Hz	$^3J_{\text{PH}_B}$, Hz
Ph	$\text{P}(\text{OMe})_3$	0.49	5.0	9.6
	PMePh_2	0.74	5.0	9.8
	PPh_3	0.81	3.9	10.7
SiMe_3	$\text{P}(\text{OMe})_3$	0.72	3.6	11.5
	PPh_3	1.01	2.0	13.7

^a Reference 66.

TABLE XIX. ^1H NMR Coupling Constants (Hz) and ν_{PH} (cm^{-1}) in *trans*- $\text{HPI}(\text{PEt}_3)_2\text{L}^+$ ^a

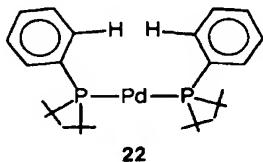
L	$^1J_{\text{PH}}$	ν_{PH}
$\text{P}(\text{OPh})_3$	872	2090
$\text{P}(\text{OMe})_3$	846	2067
PPh_3	890	2100
PEt_3	790	2090

^a J. P. Jesson, "Transition Metal Hydrides", E. L. Muetterties, Ed., Marcel Dekker, New York, N.Y., 1971, p 100.

than those observed.⁶² Interestingly, the colors of the compounds change from yellow to dark brown as L gets larger!

The methyl protons in $\text{M}(\text{CO})_5\text{P}(\text{To})_3$ complexes ($\text{M} = \text{Cr, Mo, or W}$) are shifted slightly downfield (0.04 ppm) with respect to the free phosphines in the meta and para isomers. The ortho isomers are shifted *upfield* by ~ 0.23 ppm, apparently because of proximity to the metal or carbonyl groups.⁶³ A related effect in crowded aromatic hydrocarbons⁶⁴ can be seen in the methyl chemical shifts in Figure 21.

The ortho hydrogens nearest the metal in 22 appear at unusually low field (δ 9.33).⁶⁵ The x-ray structure shows very short Pd-H distances of 2.76 ± 0.03 Å.



The chemical shift difference ($\Delta\delta$) between the inequivalent methylene protons, and the vicinal coupling constants $^3J_{\text{PH}}$ in $\text{CpFe}(\text{CO})\text{LCH}_2\text{R}$ complexes depend on the size of L (Table XVIII). Baird⁶⁶ has explained the results in terms of the effect of the sizes of R and L on the populations of the rotamers 23 to 25.

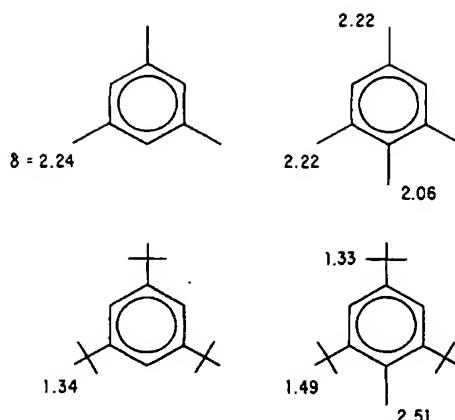
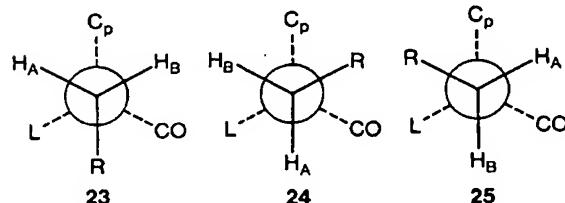


Figure 21. ^1H chemical shifts in crowded aromatic hydrocarbons, from ref 64.

TABLE XX. ^{13}C NMR Data^a for Carbonyl Carbons in $\text{CpMn}(\text{CO})_2\text{L}$

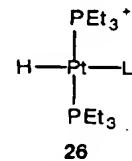
L	$\delta(^{13}\text{CO})$, ppm	$^2J_{\text{PC}}$, Hz
$\text{P}(\text{OPh})_3$	228.8	36
$\text{P}(\text{OMe})_3$	229.5	34
PPh_3	232.8	23
PBu_3	231.1	26

^a G. M. Bodner, *Inorg. Chem.*, 13, 2563 (1974).



With the largest R and L (bottom of Table XVIII), essentially only rotamer 23 is populated. The large difference between $^3J_{\text{PH}_A}$ and $^3J_{\text{PH}_B}$ suggests that one is a gauche coupling, the other a trans. 23 is most likely because R is gauche to only one bulky group (L) whereas it is gauche to two (L and Cp) in 25. With smaller L (or R), rotamers 24 and 25 can be appreciably populated so that $^3J_{\text{PH}_A}$ (which is an average over rotamers) increases while $^3J_{\text{PH}_B}$ decreases. The explanation is supported by temperature studies.

Values of $^1J_{\text{PH}}$ in *trans*- $\text{HPI}(\text{PEt}_3)_2\text{L}^+$ complexes 26 (Table XIX) tend to increase for more electronegative L. However PPh_3 ,



the largest ligand, is out of line. The large $^1J_{\text{PH}}$ implies an exceptionally strong trans Pt-H bond. This complex also has the highest Pt-H stretching frequency of the series.

4. ^{13}C Chemical Shifts and Coupling Constants

A series of ligands similar to that in Table XIX was used in a study of ^{13}C NMR chemical shifts and coupling constants in $\text{CpMn}(\text{CO})_2\text{L}$ complexes (Table XX). Again PPh_3 is out of line; $^2J_{\text{PC}}$ is abnormally low.

TABLE XXI. Infrared Stretching Frequencies of ν_{IrH} ^a in $\text{HirCl}_2(\text{CO})\text{L}_2$ Complexes

L	ν_{IrH} , cm^{-1}	L	ν_{IrH} , cm^{-1}
PMe_3	2169	$\text{PPr}_2(t\text{-Bu})$	2242
PMe_2Ph	2191	$\text{PBu}_2(t\text{-Bu})$	2244
$\text{PMe}_2(t\text{-Bu})$	2208	$\text{PMe}(t\text{-Bu})_2$	2254
PMePh_2	2217	PCy_3 ^b	2276
$\text{PEt}_2(t\text{-Bu})$	2227	$\text{PEt}(t\text{-Bu})_2$	2300
PPh_3	2237	$\text{PPh}(t\text{-Bu})_2$	2300

^a From ref 67 unless noted otherwise. ^b F. G. Moers, J. A. M. deJong, and P. M. H. Beaumont, *J. Inorg. Nucl. Chem.*, **35**, 1915 (1973).

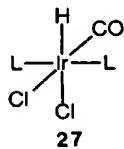
TABLE XXII. P=O Stretching Frequencies in Oxides

Compound	$\nu_{\text{P=O}}$, cm^{-1}
$\text{OP}(\text{OCH}_2)_3\text{CC}_6\text{H}_11$	1327 ^a
$\text{OP}(\text{OBu})_3$	1260 ^b
$\text{OP}(\alpha\text{-C}_6\text{H}_4)_3\text{N}$	1250 ^c
$\text{OP}(\alpha\text{-C}_6\text{H}_4)_3\text{CH}$	1240 ^d
$\text{OP}(\alpha\text{-C}_6\text{H}_4)_3\text{PO}$	1233 ^d
OPPh_3	1195 ^f

^a L. J. Vande Griend and J. G. Verkade, private communication from Verkade. ^b S. C. Goodman and J. G. Verkade, *Inorg. Chem.*, **5**, 498 (1966). ^c D. Hellwinkel and W. Schenk, *Angew. Chem. Int. Ed. Engl.*, **8**, 987 (1969). ^d Reference 42. ^e Reference 42. ^f F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960).

B. Infrared Frequencies and Intensities

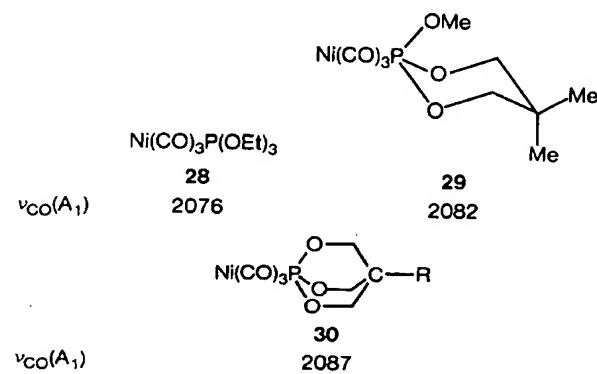
Changes in bonding as a result of increasing ligand size can be expected to affect vibrational spectra. One of the most striking examples is Shaw's⁶⁷ observation of an increase in ν_{IrH} in the series of complexes of type 27 in Table XXI.



The equilibrium constant for going to the six-coordinate complex (27) in eq 3 decreases as L becomes larger,⁶⁷ even though some of the larger ligands are better donors. Apparently the IrH bond becomes stronger going down the table; the Ir-P bonds must become weaker in the same order.



The carbonyl stretching frequencies in 28, 29, and 30 show the effect of increasing constraints on reducing the metal

TABLE XXIII. Relative IR Intensities^a in $\text{Mn}_2(\text{CO})_9\text{L}$

L	I_1/I_2	L	I_1/I_2
PF_3	0.05	PBu_3	0.3
$\text{P}(\text{OPh})_3$	0.3	PPh_3	0.6

^a J. P. Fawcett, A. J. Poë, and M. V. Twigg, *J. Organomet. Chem.*, **61**, 315 (1973).

TABLE XXIV. Angles (α) between CO Groups, and CO Stretching Force Constants in $\text{PzB}(\text{Pz})_3\text{Mn}(\text{CO})_2\text{L}$ Complexes^a

L	α , deg	k_{CO} , mdyn/ \AA
PCl_3	44.4	15.54
$\text{P}(\text{OPh})_3$	45.6	15.08
PBu_3	46.9	14.46
PPh_3	43.8	14.80
PCy_3	42.7	14.40

^a From ref 69.

electron density in $\text{Ni}(0)$ compounds.⁶⁸ (This is also reflected in a reduced basicity of the NiL_4 complexes toward H^+ .)

The P=O stretching frequencies of the oxides of phosphorus ligands (Table XXII) show similar effects. Note the decrease in frequency in the triptycene derivatives as the covalent radius of the bridgehead atom is increased in size.

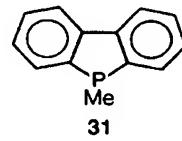
The relative IR intensities of the two highest frequency carbonyl stretching modes ν_1 and ν_2 in $\text{Mn}_2(\text{CO})_9\text{L}$ depend on the size of L (Table XXIII). The larger ligands may increase the PMnC angle.



Schoenberg and Anderson⁶⁹ have used the relative intensities of symmetric and asymmetric carbonyl vibrations in $\text{PzB}(\text{Pz})_3\text{Mn}(\text{CO})_2\text{L}$ complexes to calculate angles (α) between the CO groups (Table XXIV). Larger ligands decrease α , increasing the symmetric to asymmetric intensity ratio. The CO force constants show the expected dependence on electronic effects.

Steric effects can change the number of bands observed in the IR. $\text{M}(\text{CO})_5\text{L}$ complexes of Cr, Mo, and W show a single E carbonyl mode (at about 1945 cm^{-1}) when $\text{L} = \text{P}(p\text{-Tol})_3$ or $\text{P}(m\text{-Tol})_3$. With $\text{P}(o\text{-Tol})_3$, however, the band is split into a doublet with a separation of $\sim 10 \text{ cm}^{-1}$.⁶³

The $\text{Ni}(\text{CN})_2\text{L}_3$ complex ($\text{L} = 5\text{-methyl-5H-dibenzophosphole}$, 31) shows three CN stretching bands in its null IR spectrum at



2118 , 2108 , and 2102 cm^{-1} .⁷⁰ Its 5-ethyl analogue shows only one, at 2118 . The UV absorption spectra of the crystals are also very different. A single-crystal x-ray study shows that the compounds have different stereochemistries: square pyramidal 32 (5-Me) and trigonal-bipyramidal 33 (5-Et).

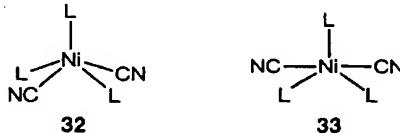


TABLE XXV. Effect of Replacing $P(n\text{-Pr})_3$ by $P(i\text{-Pr})_3$ on Spectra of $\text{trans-NiX}_2\text{L}_2$ ^a

Band	$-\Delta\nu, \text{cm}^{-1}$		
	X = NCS	Cl	Br
III	600	1400	1750
IV		1250	1350

^a From ref 72.

C. Electronic Spectra

Dobson, Stoltz, and Sheline, in their review of group 6B metal carbonyl derivatives, point out that derivatives with small phosphines are often colorless, while those of larger ones are yellow.^{71a} The deepening of color of $[(\text{CH}_3\text{OH})\text{Co}(\text{DH})_2\text{L}]^+$ complexes as the size of L increases was mentioned previously.

Bennett and co-workers^{71b} found a red shift of the lowest frequency ligand field band in $\text{trans-}[\text{CrL}_2(\text{NCS})_4]^{2-}$ complexes in a sequence which must involve ligand size: PMe_3 (19 950), PEt_3 (19 500), and PEt_2Ph (19 050 cm^{-1}). Complexes with bulkier ligands PPh_3 and PCy_3 could not be made.

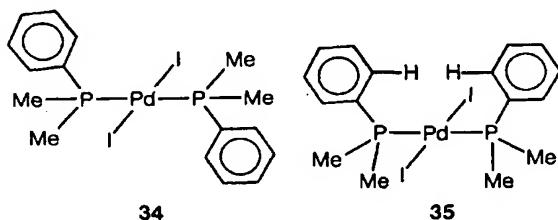
Electronic transitions of $\text{trans-NiX}_2\text{L}_2$ complexes show a marked red shift when $P(n\text{-Pr})_3$ is replaced by $P(i\text{-Pr})_3$. The frequencies of bands III and IV at $\sim 25\ 000$ and $\sim 19\ 000\ \text{cm}^{-1}$ decrease by an amount which depends on X (Table XXV). The shift is greater for larger X. The authors⁷² attribute the shifts to lengthening of the Ni-X bonds. A similar red shift has been reported more recently for the lowest frequency transition in tetrahedral NiBr_2L_2 complexes: PMePh_2 (11 680), PEtPh_2 (11 360), and $\text{PPh}_2(t\text{-Bu})$ (10 800 cm^{-1}); here, however, the effect was attributed to lengthening Ni-P bonds.⁷³ Probably both occur.

The complexes $\text{NiCl}_2(\text{PEt}_3)_2$, $\text{NiBr}_2(\text{PEt}_3)_2$, and $\text{NiCl}_2(\text{PCy}_3)_2$ are red while $\text{NiBr}_2(\text{PCy}_3)_2$ is olive green; all are diamagnetic in the solid state.⁷⁴

Ligand size can also affect the electronic spectra of NiX_2L_2 complexes in solution by shifting the square-planar-tetrahedral equilibrium, to be discussed in section IV.G.2.

Larger ligands also dissociate more readily, as we shall see in section IV.A. Thus, $\text{Ni}(\text{PMe}_3)_4$ is a light yellow crystalline solid and gives light yellow benzene solutions. $\text{Ni}(\text{PEt}_3)_4$ crystals look very similar but give permanganate violet solutions, because of a high concentration of NiL_3 .⁹ Similarly $\text{Ni}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2$ is light yellow⁹ while $\text{Ni}(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2)_2$ is violet;⁷⁵ one end of the bulky diphosphine remains uncoordinated, even in the solid.

$\text{trans-PdI}_2(\text{PMe}_2\text{Ph})_2$ exists in two crystalline modifications, one yellow (34) and one red (35).⁷⁶ 35 shows much shorter ortho H-Pd distances (2.84 vs. 3.28 Å).



D. Electric and Magnetic Dipole Moments

The electric dipole moment of paramagnetic $\text{NiI}_2(\text{PPh}_3)_2$ is 8.5 D, much larger than the 5.9 D of $\text{NiBr}_2(\text{PPh}_3)_2$.⁷⁷ This result cannot be explained in terms of the electronegativities of the halogens, but is consistent with a greater tetrahedral distortion with the larger halide.

A similarly anomalous trend is seen in the $\text{trans-CH}_3\text{Pt}(\text{PEt}_3)_2\text{X}$

TABLE XXVI. Percent s Character in Co(II) Complexes by ESR

L	$\text{Co}(\text{TPP})\text{L}^a$	$\text{Co}(\text{salen})\text{L}^b$
PF_3	68	
$\text{P}(\text{OMe})_3$	55	49
$\text{P}(\text{OEt})_3$	51	
$\text{P}(\text{OBu})_3$	48	
PMe_3	36	33
PHMe_2	34	
PBu_3	31	
PMe_2Ph	28	
PEt_3	27	
PPh_3		24

^a B. B. Wayland and M. E. Abd-Elmageed, *J. Am. Chem. Soc.*, **96**, 4809 (1974). ^b B. B. Wayland, M. E. Abd-Elmageed, and L. F. Mehne, *Inorg. Chem.*, **14**, 1456 (1975).

TABLE XXVII. UV Photoelectron Data on Gaseous Ligands

L	IP_1, eV	L	IP_1, eV
PH_3	10.58 ^a	PBu_3	8.11 ^b
$\text{P}(\text{OCH}_2)_3\text{CEt}$	9.8 ^b	$\text{P}(\text{i-Pr})_3$	8.05 ^b
$\text{P}(\text{OMe})_3$	9.25 ^a	$\text{P}(\text{t-Bu})_3$	7.71 ^b
PMe_3	8.65 ^a	$\text{P}(\text{m-C}_6\text{H}_4\text{F})_3$	8.32 ^c
$\text{P}(\text{vinyl})_3$	8.48 ^b	PPh_3	7.92 ^c
PEt_3	8.31 ^b	$\text{P}(\text{p-C}_6\text{H}_4\text{OCH}_3)_3$	7.48 ^c

^a O. Stelzer and E. Unger, *Chem. Ber.*, **108**, 1246 (1975). ^b M. A. Weiner and M. Lattman, private communication from Weiner. ^c M. A. Weiner, M. Lattman, and S. O. Grim, *J. Org. Chem.*, **40**, 1292 (1975).

series where $\mu = 3.4\ \text{D}(\text{Cl})$, $3.7(\text{Br})$, and $4.1(\text{I})$, or in $\text{trans-CH}_3\text{Pt}(\text{PEt}_3)_2\text{X}$, where $\mu = 3.7(\text{Cl})$ and $4.15(\text{I})$.⁷⁸ The anomaly should be small or absent in $\text{trans-CH}_3\text{Pt}(\text{PMe}_3)_2\text{X}$. An effect of $\text{P}(\text{t-Bu})_3$ angle on electric dipole moment is seen in comparing $\text{cis-Ph}_2\text{Pt}(\text{PEt}_3)_2$ (7.2) and $\text{cis-Ph}_2\text{Pt}(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)$ (8.4 D).⁷⁸

The magnetic dipole moment of $\text{NiP}(\text{t-Bu})_3\text{I}_3^-$ (3.07 BM) is anomalously small when compared to $\text{NiPPh}_3\text{I}_3^-$ (3.46).⁷⁹ The corresponding complexes with the smaller bromide ion, which are less crowded, show essentially the same moments for $\text{P}(\text{t-Bu})_3$ (3.73) and PPh_3 (3.68) complexes.⁸⁰

E. Electrochemistry and ESR

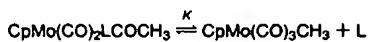
Steric effects in electrochemistry have barely been explored. Baird^{81a} has found that the Co(II) complexes $\text{Co}(\text{salen})\text{L}_2^+$ and $\text{Co}(\text{DHL}_2)_2^+$ become easier to reduce in the order of increasing ligand size: $\text{PMe}_2\text{Ph} < \text{PBu}_3 < \text{PMe}_2\text{Ph} < \text{PPh}_3$.

Electrochemical studies on oxidation of $\text{M}(\text{CO})_2[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]_2$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) show that the complexes with $n = 1$ are more easily oxidized than those with $n = 2$.⁸²

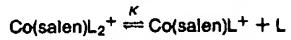
ESR studies on Co(II) phosphine complexes (Table XXVI) show that the percent s character in the P-donor orbital generally increases with more electronegative substituents on P. Large substituents, however, show abnormally low s character, most clearly seen for PPh_3 .

F. Ionization Potentials of Free Ligands

The advent of UV photoelectron spectroscopy has made it possible to measure ionization potentials with high accuracy. The first ionization potential (IP_1) of free phosphorus ligands nearly always arises from the phosphorus lone pair. It might be expected that electron-withdrawing groups would increase IP_1 , which is indeed the case (Table XXVII). Going from $\text{P}(\text{p-C}_6\text{H}_4\text{OCH}_3)_3$ to $\text{P}(\text{m-C}_6\text{H}_4\text{F})_3$ increases IP_1 by 0.84 eV. The data in Table XXVII suggest, however, that there is also an important steric effect on IP_1 . Thus, the ionization potential decreases in the series PMe_3 , $\text{P}(\text{vinyl})_3$, and $\text{P}(\text{m-C}_6\text{H}_4\text{F})_3$ even though the substituents on P become more electronegative. This and the

TABLE XXVIII. Equilibrium Constants^a in CH₃CN at 60 °C for the Reaction

L	K × 10 ⁴ , M	L	K × 10 ⁴ , M
PM ₂ Ph	0.1	PPh ₃	8.3
PBu ₃	0.3	PCy ₃	50
PM ₂ Ph ₂	1.3	PPh ₂ (i-Pr)	90
P(p-C ₆ H ₄ OCH ₃) ₃	5.3	P(o-Tol)	b
P(p-Tol) ₃	6.1		

^a From ref 88. ^b Very large.TABLE XXIX. Equilibrium Constants^a in 95% EtOH at 25 °C for the Reaction:

L	K × 10 ⁴ , M	L	K × 10 ⁴ , M
PM ₂ Ph	0.13	PM ₂ Ph ₂	9.1
PBu ₃	3.7	PPh ₃	610

^a From ref 81.

marked decrease in IP_1 in the series PH₃, PMe₃, PEt₃, P(i-Pr)₃, and P(t-Bu)₃ can be largely attributed to the decreasing percentage of s character in the lone pair as larger substituents force open the SPS angles. The high ionization potential of P(OCH₂)₃CEt relative to P(OMe)₃ is consistent with a smaller OPO angle in the cage.

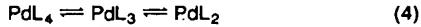
IV. Rates and Equilibria

Ligand size can have a marked influence on rates and equilibria. This section will emphasize quantitative solution studies on simple reactions. Section V deals with the isolation of unusual complexes and section VI with homogeneous catalytic systems.

A. Dissociation of Phosphorus Ligands

We saw earlier (Table II) that steric effects dominate the dissociation equilibria of NiL_4 complexes. K_d at 25 °C increases by a factor of 10⁸ on going from P(O-p-Tol)₃ to P(O-o-Tol)₃, an increase in Θ from 128 to 141°. This corresponds to a decrease in ΔH_d of 10 kcal/mol.⁹ The rates of L dissociation also show a steric effect; k_d is 100 to 1000 times faster for P(O-o-Tol)₃ than for P(O-p-Tol)₃ at 25 °C. Electronic effects are also important; phosphines dissociate faster from Ni(0) than phosphites of similar size.⁹

Musco and co-workers^{83,84} have studied the equilibria

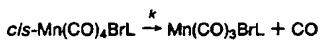


and find that the extent of L dissociation is dominated by steric effects, increasing in the order PMe₃ ~ PMe₂Ph ~ PMePh₂ < PEt₃ ~ PBu₃ ~ PPh₃ < PB₃ < P(i-Pr)₃ < PCy₃ < PPh₂(i-Bu)₂.⁸³ NMR studies⁸⁴ also show steric effects on the rates of exchange of free and coordinated phosphines.

Vapor pressure osmometry shows that L dissociation from CuXL₃ (X = halogen) increases in the steric order PMe₂Ph ~ PMePh₂ < PPh₃ and AsMe₂Ph < AsMePh.⁸⁵ CuX(AsPh₃)₃ could not be made.

Equilibrium constants of Barnett and Pollmann⁸⁶ for L dissociation from CpMo(CO)₂LCOCH₃ are shown in Table XXVIII. P(o-Tol)₃, the largest ligand used in the study, is completely dissociated.

Equilibrium constants for L dissociation from Co(salen)L₂⁺ (Table XXIX) show a larger steric effect; K increases by a factor of 4700 from PMe₂Ph to PPh₃. Activation energies for disso-

TABLE XXX. Relative Rate Constants^a in CHCl₂CHCl₂ at 40 °C for the Reaction:

L	k_{rel}	L	k_{rel}
P(OBu) ₃	0.3	PBu ₃	1.3
SbPh ₃	0.6	AsPh ₃	2.3
P(OPh) ₃	0.6	PPh ₃	8.4
CO	(1.0)		

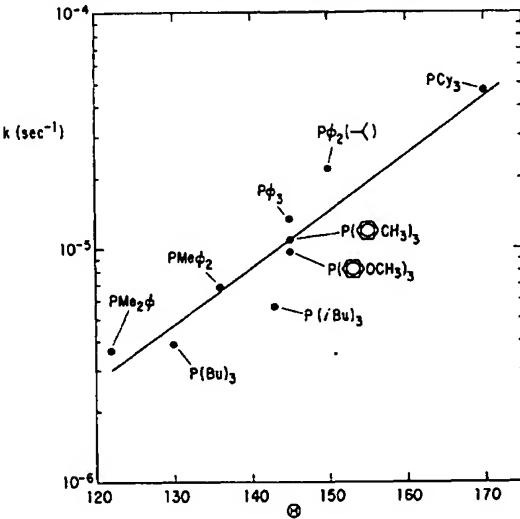
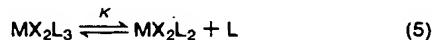
^a J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.*, **98**, 3155 (1976).

Figure 22. Rate constants in CH₃CN at 60 °C for the reaction: $\text{CpMo}(\text{CO})_2\text{LCOCH}_3 \rightarrow \text{CpMo}(\text{CO})_2\text{LCH}_3 + \text{CO}$, from ref 86.

ciation (24.7 kcal/mol for PMe₂Ph and 14.9 for PMePh₂ (determined by NMR line shapes) show a marked steric labilization.⁸¹

Rates of dissociation of HCoL₄ complexes increase in the steric order P(OMe)₃ < P(OEt)₃ < P(OPh)₃,⁸⁷ equilibrium mixtures in competition experiments strongly favor the smaller phosphites.

Rigo and Turco⁸⁸ have concluded that steric effects dominate equilibria of type



where M = Ni or Co and X = CN or halogen. We have confirmed this in the nickel dicyanide system and find that K_5 increases in the sequence PMe₃ < PEt₃ < PCy₃.⁸⁹

The extent of L dissociation will, of course, depend on the steric requirements of the other ligands in a complex. We find a reduced tendency to dissociate L in the analogous HNiL₃CN complexes,⁹⁰ presumably because H is less sterically demanding than CN. The extent of phosphine dissociation is less for HRuCl(PPh₃)₃ than for RuCl₂(PPh₃)₃,⁹¹ presumably for a similar reason.

B. Dissociation of Other Ligands

CO substitution in *cis*-MnBr(CO)₄L involves rate determining loss of the CO cis to both Br and L. Relative rates (Table XXX) increase with the size of phosphorus ligand and in the order SbPh₃ < AsPh₃ < PPh₃.

Figure 22 shows the effect of increasing the size of L on the rates of CO dissociation from CpMo(CO)₂LCOCH₃. A small electronic effect is evident in the increase in rate on going from P(p-C₆H₄OCH₃)₃ to PPh₃. Rates of chelation of (R₂P-

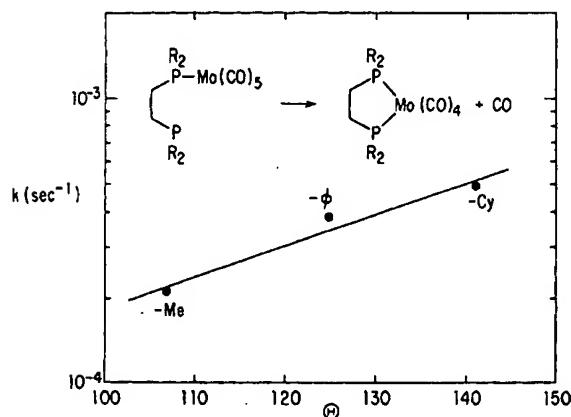


Figure 23. Rate constants for ring closure in nonane at 110 °C, from ref 92.

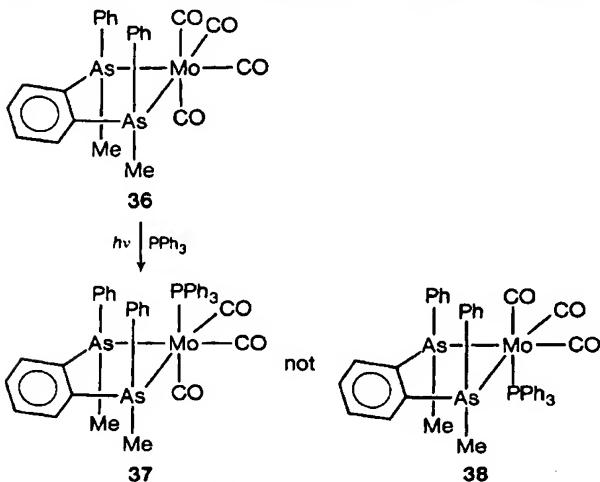
$\text{CH}_2\text{CH}_2\text{PR}_2\text{Mo}(\text{CO})_5$ complexes⁹² (Figure 23) increase with the size of R, but the slope is less. Steric acceleration can be understood in terms of a rate-determining loss of CO, followed by rapid ring closure. The rates of chelation of $[\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2]\text{Cr}(\text{CO})_5$ complexes also depend on the value of n (Table XXXI).

Herskovitz⁹³ has found that the dissociation constants for eq 6 and 7 increase in the sequence R = Me < Et < i-Pr, obviously a case of steric control.



Reversible CO dissociation from $\text{CoX}_2\text{L}_2(\text{CO})$ complexes increases with the size of L (Table XXXII). The dissociation sequence NCS < Br < Cl must involve both electronic and steric factors, since Br is larger than Cl. The authors⁹⁴ argued against steric effects of L on the basis that earlier work⁹⁵ on MX_2L_3 dissociation showed that differences in K were due to differences in ΔH_d , not ΔS_d . We now know that steric effects can have a major influence on ΔH_d .⁹

Steric factors can influence rates of radiation-induced dissociation reactions. Irradiation of 36 in the presence of PPh_3 gives 37 rather than the less crowded 38,⁹⁶ indicating more rapid



loss of CO from the most hindered position. The preferential kinetically controlled formation of *cis*- $\text{M}(\text{CO})_4\text{L}_2$ complexes in light-induced reactions of $\text{M}(\text{CO})_5\text{L}$ with L may be largely sterically controlled.

TABLE XXXI. Rate Constants^a in *n*-Octane at 124 °C for the Reaction: $(\text{diphosphine})\text{Cr}(\text{CO})_5 \rightarrow \text{CO} + \text{chelated} (\text{diphosphine})\text{Cr}(\text{CO})_4$

Diphosphine	$10^4 k, \text{ sec}^{-1}$
$\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$	0.75
$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$	26
$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$	34
$\text{Ph}_2\text{PCH}_2\text{PPh}_2$	55

^a J. A. Connor, J. P. Day, E. M. Jones, and G. K. McEwen, *J. Chem. Soc., Dalton Trans.*, 347 (1973).

TABLE XXXII. Equilibrium Constants^a in $\text{C}_2\text{H}_4\text{Cl}_2$ at 25 °C for the Reaction: $\text{CoX}_2\text{L}_2(\text{CO}) \rightleftharpoons \text{CO} + \text{CoX}_2\text{L}_2$

L	$\text{X} = \text{NCS}$	Br	Cl
PEt_3		4.0	8.1
$\text{P}(\text{i-Pr})_3$		4.3	12.7
PEt_2Ph		10	500
PEtPh_2	20	97	1470
PPh_3	110	3000	^b
PCy_3	450	^b	^b

^a From ref 94. ^b Very large.

$\text{RuBr}_2[\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2]_2$ in 1,2-dichloroethane dissociates to Br^- and $\text{RuBr}[\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2]_2^+$. Less crowded $\text{RuX}_2[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]_2$ complexes with $n = 1$ or 2 do not, nor does the complex with $n = 3$ and $\text{X} = \text{Cl}$.⁹⁷ Attempts to prepare the $n = 4$ complex $\text{RuCl}_4[\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2]_2$ failed, giving instead $\text{RuCl}_4[\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2]_3$.

C. Metal-Metal Bond Cleavage

A special class of dissociation reactions involves cleavage of metal-metal bonds. Drakesmith and Whyman⁹⁸ have found that $\text{Ir}_4(\text{CO})_4\text{L}_3$ clusters are much more easily broken down under CO and H_2 pressure with $\text{L} = \text{PPh}_3$ or $\text{P}(\text{i-Pr})_3$ than with PEt_3 , PPr_3 , or PBu_3 . Since $\text{Hlr}(\text{CO})_3\text{P}(\text{i-Pr})_3$ forms so easily, the $\text{P}(\text{i-Pr})_3$ system is particularly active in olefin hydroformylation.⁹⁹

RuX_2L_n (X = halogen, $n = 2, 3$, or 4) complexes participate in several equilibria to form binuclear complexes linked by two or three halide bridges. Only with bulky phosphines such as PPh_3 or $\text{P}(\text{p-Tol})_3$ are the mononuclear species favored; then RuX_2L_4 complexes are completely dissociated in solution to RuX_2L_3 and L .¹⁰⁰

Poë¹⁰¹ has reported that activation energies for homolytic cleavage of the Mn-Mn bond decrease in the sequence $(\text{CO})_5\text{Mn}-\text{Mn}(\text{CO})_5 > (\text{CO})_5\text{Mn}-\text{Mn}(\text{CO})_4\text{L} > \text{L}(\text{CO})_4\text{Mn}-\text{Mn}(\text{CO})_4\text{L}$ and $\text{L} = \text{P}(\text{OPh})_3 > \text{PBu}_3 > \text{PPh}_3$, suggesting a weakening of the metal-metal bond by crowding transmitted through the carbonyls.

Sufficiently large ligands should stabilize odd-electron mononuclear fragments. Indeed, while $[\text{P}(\text{OMe})_3]_4\text{Co}-\text{Co}[\text{P}(\text{OMe})_3]_4$ is a stable diamagnetic dimer,¹⁰² $\text{Co}[\text{P}(\text{OMe})_3]_4$ exists as a paramagnetic monomer,¹⁰² as do $\text{Co}[\alpha\text{-C}_6\text{H}_4(\text{PEt}_2)_2]_2$ ¹⁰³ and $\text{Co}(\text{N}_2)(\text{PPh}_3)_3$.¹⁰⁴ Steric crowding probably accounts for why $\text{V}(\text{CO})_6$ does not dimerize and thus provides one of the rare examples of a stable paramagnetic carbonyl complex.¹⁰⁵ $\text{V}(\text{dmpe})_3$ has also been prepared.¹⁰⁶ Steric hindrance to radical recombination is a well-established phenomenon in organic chemistry.¹⁰⁷

D. Associative Reactions

The rate of carbonyl substitution on 39 by L to give 40 in Table XXXIII depends on L and is cleanly second order, implying an associative reaction. There is an electronic factor in the rate

TABLE XXXIII. Rate Constants^a in Toluene for the Reaction:
 $39 + L \xrightarrow{k} 40 + CO$

L	$10^4 k_2, s^{-1} M^{-1}$	T, °C
PBu ₃	12.3	30
PEt ₂ Ph ₂	9.6	35
PPh ₂	8.5	35
P(OMe) ₃	1.23	35
PPh ₃	0.65	35
PCy ₃	0.58	35
P(OPh) ₃	0.069	35
P(<i>o</i> -Tol) ₃	^b	70

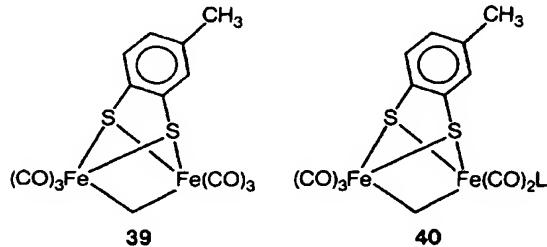
^a P. C. Elgen and J. N. Gerlach, *Inorg. Chem.*, 12, 2526 (1973). ^b No reaction in 140 h.

TABLE XXXIV. Rate Constants^a in Decalin at 50 °C for the Reaction of Ru₃(CO)₁₂ with L

L	$10^4 k_2, s^{-1} M^{-1}$	L	$10^4 k_2, s^{-1} M^{-1}$
PBu ₃	456	P(OPh) ₃	17
P(OEt) ₃	191	PPh ₃	13
P(OCH ₂) ₃ C ₂ H ₅	161	PCy ₃	<1

^a From ref 108.

constants; the phosphites react more slowly than expected on the basis of size alone. P(*o*-Tol)₃ fails to react at all, even under forcing conditions.



Pöö and Twigg¹⁰⁸ have shown that the second-order rate term in the reaction of L with Ru₃(CO)₁₂ (Table XXXIV) depends on both electronic and steric effects. PPh₃ and especially PCy₃ react more slowly than expected on the basis of a plot of log k₂ against half-neutralization potentials. A number of other systems show the same behavior: Co(NO)(CO)₃, Fe(NO)₂(CO)₂, Mn(NO)(CO)₄, CpRh(CO)₂, and M(CO)₆ (M = Cr, Mo, and W).¹⁰⁸

¹H NMR line shape effects indicate slow ligand exchange with HPdCl(PCy₃)₂ but fast exchange with the less crowded HPdCl(PCy₃)(PBu₃) and HPdCl(PBu₃)₂.¹⁰⁹ We have similarly found slow associative exchange of PCy₃ with HNi(PCy₃)₂CN, but a very fast reaction of PEt₃ with HNi(PEt₃)₂CN (by ³¹P NMR).⁹⁰

Competitive rate constants for reactions of the carbene intermediate Fe(CO)₃C(OEt)Me with various L relative to PPh₃ are shown in Table XXXV. The discrimination of this uncrowded species is very small. P(OPh)₃ reacts more slowly than expected on the basis of size alone.

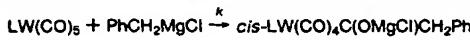
Another type of associative reaction is the formation of carbenes by the reaction of LW(CO)₅ with PhCH₂MgCl (Table XXXVI), where the steric effect is larger (the ratio of PBu₃ to PCy₃ rates is 6.0). For a given L, rates decrease in the order W ≈ Mo > Cr, consistent with more crowding on a smaller metal.

Rates of reaction of LW(CO)₅ with (MeLi)₄ to give *cis*-LW(CO)₄C(OLi)Me are first order in W and one-fourth order in (MeLi)₄, implying formation of monomeric MeLi prior to nucleophilic attack.¹¹⁰ Rate constants in Table XXXVII show a smaller steric effect than those in Table XXXVI, consistent with the smaller size of MeLi compared to PhCH₂MgCl.

TABLE XXXV. Competitive Rate Constants^a in Heptane at ~70 °C in the Reactions:

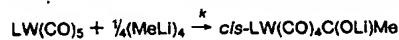
L	k_2/k_{-1}
PBu ₃	3.0
PCy ₃	1.0
P(OPh) ₃	0.3

^a D. J. Daresbourg and H. L. Conder, *Inorg. Chem.*, 13, 374 (1974).

TABLE XXXVI. Rate Constants^a in THF at 27 °C for the Reaction:

L	$10^3 k, s^{-1} M^{-1}$	L	$10^3 k, s^{-1} M^{-1}$
P(OEt) ₃	25.7	PBu ₃	8.5
PM ₃	19.1	PPh ₃	5.0
PM ₂ Ph	14.0	PCy ₃	1.42
PM ₂ Ph ₂	10.4	P(<i>o</i> -Tol) ₃	1.75 ^b

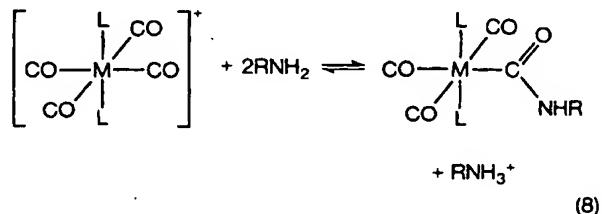
^a M. Y. Daresbourg, H. L. Conder, D. J. Daresbourg, and C. Hasday, *J. Am. Chem. Soc.*, 95, 5919 (1973). ^b The product was exclusively the trans isomer.

TABLE XXXVII. Rate Constants^a in Et₂O at 25 °C for the Reaction:

L	$10^2 k, s^{-1} M^{-1/4}$	L	$10^2 k, s^{-1} M^{-1/4}$
P(OPh) ₃	6.56	PPh ₃	3.96
PBu ₃	4.74	PCy ₃	2.27

^a From ref 110.

A kinetic and equilibrium study¹¹¹ of carbamoyl complex formation (eq 8) from Mn and Re carbonyls showed that the rate



decreases in the order: PMePh₂ > PMe₂Ph > PPh₃. The order of the first two is expected from electronic factors but the rate with PPh₃ is abnormally slow, suggesting steric inhibition of the associative reaction. The rate also decreases with increasing bulk of the amine in the order R = *sec*-Bu > *t*-Pr > Cy > *t*-Bu, and decreasing the size of the metal from Re to Mn. Equilibrium constants decrease with increasing bulk of phosphine or amine.

Rates of reaction of KH with HCoL₄ complexes decrease in the order P(OMe)₃ > P(OEt)₃ > P(OPh)₃.⁸⁷

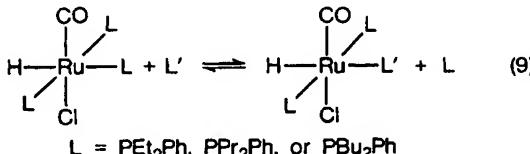
E. Ligand Exchange Equilibria

There are many situations where ligands compete for coordination sites on a transition metal. It was a study² of competition equilibria among phosphorus ligands for Ni(0) which first led me to realize the importance of steric effects. Ligand exchange in eq 9 shows a bonding order L' = P(OMe)₂Ph > PMe₂Ph ~ P(OEt)₃ > PEt₃ > PEt₂Ph ~ PPr₂Ph ~ PBu₂Ph > AsMe₂Ph > AsEt₂Ph.¹¹²

TABLE XXXVIII. Equilibrium Constants* In Hexane for the Reaction:
 $cis\text{-Mo}(\text{CO})_4(\text{PPh}_3)(\text{NHC}_5\text{H}_{10}) + \text{L} \rightleftharpoons cis\text{-Mo}(\text{CO})_4(\text{PPh}_3)\text{L} + \text{NHC}_5\text{H}_{10}$

L	K	T, °C
PPh ₃	~30	25
AsPh ₃	1.9	36.5
P(<i>o</i> -Tol) ₃	<0.09	25

* C. L. Hyde and D. J. Daresbourg, *Inorg. Chem.*, **12**, 1288 (1973).



With the exception of P(OEt)₃, the order of the phosphorus ligands is that of increasing Θ . The PPh₃ in (*o*-Tol)NiBr(PPh₃)₂ is quantitatively replaced by PMePh₂, which in turn is replaced by PMe₂Ph.¹¹³ Larger phosphines, P(*o*-Tol)₃ and P(*o*-C₆H₄OCH₃)₃ do not react. P(*i*-Pr)₃ and PCy₃ in Cr(CO)₄C(OMe)Me₃ are displaced by PEt₃ or PBu₃.¹¹⁴ A greater degree of substitution occurs when P(OMe)₃ reacts with H₂Fe(PMePh₂)₄ than when it reacts with H₂Fe[P(OEt)₃]₄.¹¹⁵

The length of the methylene chain in chelating diphosphines markedly affects their coordinating ability. ³¹P studies¹¹⁶ of competition for coordination to Ni(0) show decreasing bonding ability in the order Ph₂P(CH₂)₃PPh₂ ~ Ph₂P(CH₂)₂PPh₂ > Ph₂P(CH₂)₄PPh₂ > Ph₂PCH₂PPh₂. The last may have an inadequate bite.

Competition of phosphorus ligands with ligands of other types is also strongly influenced by the size of L. One of the best studied other ligands is CO. Figure 9 showed the results for Ni(0). Reimann and Singleton¹¹⁷ have studied the reactions of ReBr(CO)₅ with 15 different phosphorus ligands and have found that rates and equilibria of CO substitution are controlled by the size of L. For example, PEt₃ and PEtPh₂ give equilibrium mixtures of ReBr(CO)₃L₂ and ReBr(CO)₂L₃, while PPh₃ gives only disubstitution. MnBr(CO)₅ behaves similarly except that trisubstitution is even more difficult on the smaller metal. MnBr(CO)L₄ can be made with the very small ligand P(OMe)₃.¹¹⁸

Complexes of weakly held ligands can be favored by increasing the size of the phosphines. Thus Ni(PEt₃)₄ forms an N₂ complex $[(\text{N}_2)\text{Ni}(\text{PEt}_3)_3]$ in solutions under nitrogen,¹¹⁹ because a phosphine dissociates readily to form a coordinatively unsaturated 16-electron complex. Ni(PMe₃)₄ shows no tendency to dissociate an L or to coordinate N₂. An N₂ complex forms in the cyclohexylphosphine-nickel system, but the Ni is three-coordinate in an N₂ bridged dimer: N₂[Ni(PCy₃)₂]₂.¹²⁰

Electronic factors are also involved in the formation of N₂ complexes, which require a metal with very good back-bonding ability. Thus Pd(PEt₃)₃ and Pt(PEt₃)₃ do not form a detectable amount of N₂ complex at 50 psig, nor does Ni[P(O-O-Tol)₃]₃.¹¹⁹

Nitriles do coordinate to Ni(0) complexes containing phosphites.¹²¹ The equilibrium constant for eq 10 with L = P(O-*o*-Tol)₃ is ~10 at 25 °C. With L = P(O-*p*-Tol)₃, K is too small to be readily measured ($\sim 10^{-7}$). {These values were estimated from the equilibrium constants¹²¹ for CH₃CN + Ni[P(O-*o*-Tol)₃]₃ ⇌ (CH₃CN)Ni[P(O-*o*-Tol)₃]₃ at various temperatures and the known NiL₄ dissociation constants.⁹}



Equilibrium 11 lies far to the left for R = H, but far to the right for R = Me, *i*-Pr, or Ph.¹²² The HCoL₄ complexes can be prepared from the two smaller phosphites but not the larger ones.

TABLE XXXIX. Equilibrium Constants* In Toluene at 35.4 °C for the Reaction:
 $\text{W}(\text{CO})_5(\text{NH}_2\text{Ph}) + \text{L} \rightleftharpoons \text{W}(\text{CO})_5\text{L} + \text{NH}_2\text{Ph}$

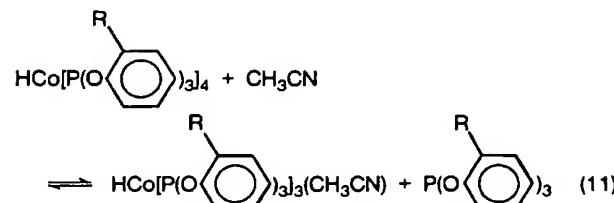
L	K	L	K
PBu ₃	225	PPh ₃	17.1
P(OCH ₂) ₃ CEt	180–360	AsPh ₃	11.2
PCy ₃	198	SbPh ₃	7.5
P(SCH ₂) ₃ CMe	45.3	P(OPh) ₃	6.6
P(OBu) ₃	31.2	BiPh ₃	1.1

* R. J. Angelici and C. M. Ingemanson, *Inorg. Chem.*, **8**, 83 (1969).

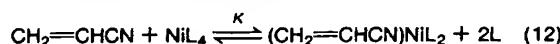
TABLE XL. Percentage of Ionic Product* In Acetone at Room Temperature for the Reaction:

L	% Ionic product
PMe ₂ Ph	15
PMePh ₂	1
PPh ₃	0
PPhCy ₂	0

* R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, **93**, 2397 (1971).



Olefins compete more effectively with smaller ligands. K's for eq 12 are about 10^4 for L = P(O-*o*-Tol)₃ and 10^{-4} for L = P(O-*p*-Tol)₃.¹²³ {An x-ray crystal structure¹²⁴ of (CH₂=CHCN)-Ni[P(O-*o*-Tol)₃]₂ shows that the acrylonitrile is indeed coordinated by its double bond.} The similarity of this 10^8 factor to the ratio of NiL₄ dissociation equilibrium constants (Table II) indicates that the strain energy in Ni[P(O-*o*-Tol)₃]₄ is completely relieved when the first P(O-*o*-Tol)₃ is removed; removal of the second ligand from NiL₃ requires essentially the same energy for L = P(O-*o*-Tol)₃ as for L = P(O-*p*-Tol)₃.



It is understandable that all known (C₂H₄)NiL₂ complexes have L's with $\Theta \gtrsim 130^\circ$. The strength of a Ni-ethylene bond is only slightly stronger than a Ni-P,¹²⁵ so smaller L's preferentially form NiL₄ complexes.

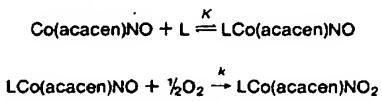
Competitions of group 5 donor ligands with piperidine and aniline are shown in Tables XXXVIII and XXXIX.

Though the K's in Table XXXIX generally decrease as the phosphorus ligand becomes more electronegative, the small P(OCH₂)₃CET does better and the large PCy₃ worse than expected on the basis of electronic effects alone. Note the order PPh₃ > AsPh₃ > SbPh₃ > BiPh₃. Recently Nasieński and co-workers¹²⁶ have pointed out that the K's are not based on true thermodynamic concentrations but rather on pseudostationary states in a photochemical reaction.

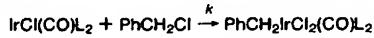
Data on competition of chloride ions with phosphines are given in Table XL (C₇H₈ = norbornadiene). The percentage of ionic product was determined by conductivity measurements.

F. Oxidative Addition Reactions

Oxidative addition in the broadest sense includes all those reactions where one or two odd-electron fragments (usually the

TABLE XLI. Equilibrium and Rate Constants^a in Acetone at 25 °C under Air at 1 Atm for the Reactions:

L	K, M ⁻¹	$10^2 k \times [O_2], \text{ s}^{-1}$
PM ₂ Ph	37	11.1
PEt ₃	23	6.67
PBu ₃	19	6.67
PEtPh ₂	5.4	5.75
P(OBu) ₃	1.87	0.8
P(OPh) ₃		No oxidation observed
PPh ₃		No oxidation observed
PCy ₃		No oxidation observed

^a From ref 130.TABLE XLII. Rate Constants^a in Benzene at 25 °C for the Reaction:

L	$k, \text{ M}^{-1} \text{ s}^{-1}$
PEtPh ₂	1.5×10^{-3}
PEt ₂ Ph	5.5×10^{-4}
P(p-C ₆ H ₄ OCH ₃)	3.3×10^{-4}
PPh ₃	1.2×10^{-4}
P(p-C ₆ H ₄ Cl)	2.0×10^{-5}

^a From ref 131.

latter, formed by cleavage of a bond in X-Y) are added to a transition metal, with an attendant increase in its formal oxidation state.¹²⁷ We can anticipate steric inhibition in direct associative reactions, and steric acceleration if prior dissociation of L or other ligand from an 18-electron complex is required as a first step.¹²⁸

Data of Halpern and Phelan¹²⁹ for the associative reaction of benzyl bromide with Co(DH)₂L are shown in Figure 24. Larger L's inhibit the reaction. There is also an electronic effect: electron-withdrawing P(p-C₆H₄Cl)₃ is slower than P(p-C₆H₄OCH₃)₃, and P(OMe)₃ falls below the line defined by the phosphines.

Rates of oxidation of Co(acacen)NO (41) with air depend on the concentration of added L, reaching a limiting value at high

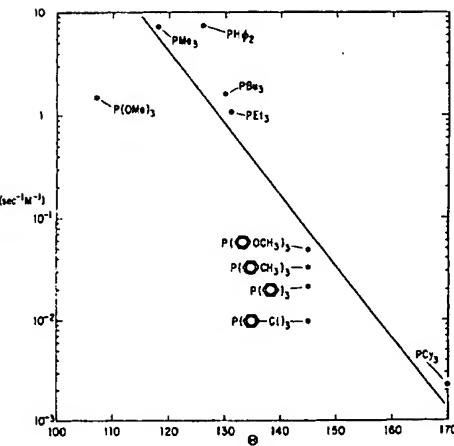
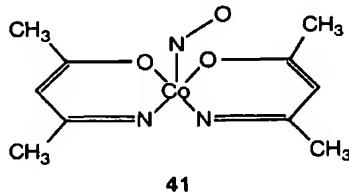


Figure 24. Rate constants in benzene at 25 °C for the reaction $2\text{Co}(\text{DH})_2\text{L} + \text{PhCH}_2\text{Br} \rightarrow \text{PhCH}_2\text{Co}(\text{DH})_2\text{L} + \text{BrCo}(\text{DH})_2\text{L}$, from ref 129.

[L].¹³⁰ Both a preassociation equilibrium constant and a rate constant (Table XLI) could be determined by analyzing the data. The ineffectiveness of PCy₃ in promoting the oxidation was attributed to its low coordinating ability. Larger size hurts both K and k, especially the former.

Ugo and co-workers¹³¹ examined electronic and steric effects of L in oxidative addition reactions of IrCl(CO)₂ complexes. Selected data are shown in Table XLII. While the effect of electron-withdrawing substituents in slowing the rate is clear, the steric effects are not obvious. Unfortunately the study was restricted to a very narrow range of ligand size (136–145°). Vaska and co-workers¹³² have recently reported results of rate and equilibrium studies which include L = PCy₃ and P(*o*-Tol)₃ (Table XLIII). Both k and K are hurt by making L very large. P(*m*-Tol)₃ acts slightly larger than P(*p*-Tol)₃. Note that the decrease in K on going from P(*m*-Tol)₃ to PCy₃ is larger for O₂ than for H₂, presumably reflecting the greater steric requirements of O₂ in the product.

While eq 13 proceeds at 0 °C when L = PMe₃, no reaction occurs when L = PEt₃.¹³³



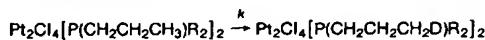
IrCl(CO)[PM₂(*t*-Bu)]₂ undergoes rapid oxidative addition with a variety of small molecules. IrCl(CO)[PEt₂(*t*-Bu)]₂ reacts much less readily, but will react with Cl₂ and O₂. IrCl(CO)[PM₂(*t*-Bu)]₂ reacts only very slowly with Cl₂ and O₂ and IrCl(CO)[PEt(*t*-Bu)]₂ does not react at all.¹³⁴

A remarkable case of steric inhibition of oxidative addition has been reported by Otsuka and co-workers.⁶⁵ Pd[PPh(*t*-Bu)₂]₂ reacts readily with O₂ to form an O₂PdL₂ complex, as expected for this highly coordinatively unsaturated complex. The still more crowded Pd[P(*t*-Bu)₃]₂ is stable in air! Apparently there is not room even for a relatively small O₂ molecule.

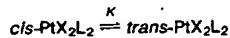
TABLE XLIII. Rate and Equilibrium Constants^a in Chlorobenzene at 30 °C for the Reaction: XY + trans-IrCl(CO)L₂ \rightleftharpoons (XY)IrCl(CO)L₂

L	XY = H ₂		XY = O ₂		XY = HCl	
	$k, \text{ s}^{-1} \text{ M}^{-1}$	$10^{-3} K, \text{ M}^{-1}$	$10^2 k, \text{ s}^{-1} \text{ M}^{-1}$	$10^{-3} K, \text{ M}^{-1}$	$k, \text{ s}^{-1} \text{ M}^{-1}$	
PPh ₃	1.2	31	5.9	28	1.1×10^4	
P(<i>p</i> -Tol) ₃	1.7	44	9.6	21	2.4×10^4	
P(<i>m</i> -Tol) ₃	0.69	25	4.4	7.0	2.7×10^3	
PCy ₃	0.0066	2.4	0.038	0.066	≤ 4.0	
P(<i>o</i> -Tol) ₃	No reaction in 3 h at 740 mm		No reaction in 18 days at 700 mm		0.79	

^a From ref 132. ^b Data in benzene.

TABLE XLIV. Rate Constants^a in $\text{CH}_3\text{COOD}/\text{D}_2\text{O}/\text{CDCl}_3$ (5/1/5) at 100 °C for the Reaction:

L	$10^4 k_{\text{obsd}}$, s^{-1}	L	$10^4 k_{\text{obsd}}$, s^{-1}
PPr_3	1.8	$\text{PPr}_2\text{t-Bu}$	4.3
PPr_2Ph	1.9	$\text{PPr}(\text{t-Bu})_2$	48
PPrPh_2	2.0		

^a from ref 138.TABLE XLV. Equilibrium Constants^a in Benzene at 25 °C for the Reaction:

L	X = Cl	X = I
PEt_3	12.3	
PPr_3	29.5	~180
PBu_3	25.5	
$\text{P}(\text{pentyl})_3$	28.4	
AsMe_2Et	55	
AsEt_3	175	
AsPr_3	~650	
AsBu_3	~340	
AsBu_2Ph	9.6	
SbEt_3	1.9	~90
SbPr_3	4.0	
SbBu_3	3.75	

^a From ref 142.

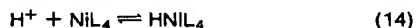
trans- $\text{RhCl}(\text{CO})[\text{PMe}_2(\text{o-C}_6\text{H}_4\text{OCH}_3)]_2$ undergoes oxidative addition with a variety of small molecules such as HCl , MeI , CCl_4 , and Cl_2 . The more crowded *trans*- $\text{RhCl}(\text{CO})[\text{P}(\text{t-Bu})_2(\text{o-C}_6\text{H}_4\text{OCH}_3)]_2$ does not react with them but rather demethylates with loss of the elements of CH_3 and Cl .¹³⁵

Rates of ortho-metallation reactions of $\text{CH}_3\text{Mn}(\text{CO})_4\text{L}$ complexes increase with the size of L in the sequence PMe_2Ph (no reaction) < $\text{P}(\text{OPh})_3$ < PPh_3 < $\text{P}(\text{o-Tol})_3$.¹³⁶ Steric acceleration of intramolecular oxidative addition reactions is now firmly established, especially by the extensive work of Shaw and co-workers.¹³⁷ Two factors are probably involved: (1) more ready dissociation of other ligands to give coordinative unsaturation, and (2) a close proximity to the metal of the bond to be broken as a consequence of steric crowding.

A study by Masters and co-workers¹³⁸ shows the effect of steric crowding on the rate of H-D exchange on C-3 of the propyl group in $\text{Pt}_2\text{Cl}_4(\text{PPrR}_2)_2$ complexes (Table XLIV).

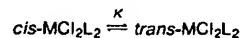
Increasing the bulk of the ligand also stabilizes four-membered ring intermediates, as shown by an increase in the rate of exchange at C-2 relative to C-3.¹³⁸

An example of the effect of structural constraints on an oxidative addition reaction is the decreasing equilibrium constants (a factor of >30) for eq 14 in the sequence $\text{L} = \text{P}(\text{OEt})_3 < \text{P}(\text{OMe}(\text{OCH}_2)_2\text{CMe}_2 < \text{P}(\text{OCH}_2)_3\text{CR}$.⁶⁸

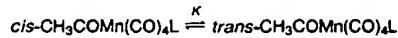


In this case, of course, the constraint reduces the electron density on nickel. A greater Ni 2p_{3/2} binding energy (0.5 eV) for $\text{Ni}[\text{P}(\text{OCH}_2)_3\text{CR}]_4$ than for $\text{Ni}[\text{P}(\text{OEt})_3]_4$ is observed by ESCA.¹³⁹

The chain length in $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ complexes can have a marked effect on reactivity. For example, $\text{Ni}[\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2]_2$ reacts with PhBr at 50 °C to give $\text{PhNiBr}[\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2]_2$ while $\text{Ni}[\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2]_2$ does not react under these conditions.¹⁴⁰ With the more reactive PhCOBr , both complexes react at 70 °C but give different products. $\text{PhCONiBr}[\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2]_2$ is stable for at least 40 h, but the more crowded $\text{PhCONiBr}[\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2]_2$ decomposes rapidly.

TABLE XLVI. Equilibrium Constants^a in Benzene at 25 °C for the Reaction:

L	M = Pd	M = Pt
SbMe_3	1.5	0.25
SbEt_3	15.7	1.9
SbPr_3	25.3	4.0
SbBu_3	26.0	3.8
SbPh_3	5.8	

^a J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 70 (1953).TABLE XLVII. Equilibrium Constants^a in Benzene at 25 °C for the Reaction:

L	K	L	K
$\text{P}(\text{OCH}_2)_3\text{CMe}$	~0 ^b	SbPh_3	~0 ^b
$\text{P}(\text{OMe})_3$	0.11	AsPh_3	0.11
PMe_2Ph	~0	PPh_3	0.42
PEt_3	~0		

^a C. S. Krahanzel and P. K. Maples, *Inorg. Chem.*, 7, 1806 (1968). ^b Too little of the trans isomer to detect.

$(\text{CH}_2)_4\text{PPh}_2$ reacts with excess PhCOBr to give a mixture of $\text{NiBr}_2[\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2]$, $\text{Ni}(\text{CO})[\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2]_2$, and PhCOPh .

$\text{Ni}[\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2]_2$ reacts readily with HCN in a 1:1 ratio to give $\text{HNiCN}[\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2]_2$ (one diphosphine monodentate).⁸⁰ $\text{Ni}[\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2]_2$ and $\text{Ni}[\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2]_2$ under the same conditions react to only a small extent.¹⁴¹

G. Isomerism

1. Cis-Trans

The most familiar cis-trans isomerism is in MX_2L_2 complexes of Pd and Pt. Table XLV shows some data published several years ago by Chatt and Wilkins¹⁴² which show that the trans/cis ratio is generally favored by bulkier L and by iodide over chloride. The stabilizing effect of the phenyl group on *cis*- $\text{PtCl}_2(\text{AsBu}_2\text{Ph})_2$ was said to be partly electronic. An earlier study of stilbene complexes by the same authors (Table XLVI) showed a marked increase in K when Me was replaced by Et, and smaller changes on going to Pr or Bu. SbPh_3 gave more *cis*- $\text{PdCl}_2(\text{SbPh}_3)_2$ than expected on the basis of size alone. The less crowded complexes gave a higher percentage of cis isomers.

Recent studies by Verstuyft and Nelson¹⁴³ on PdX_2L_2 complexes [$\text{L} = \text{PMe}_2\text{-p-C}_6\text{H}_4\text{Y}$ or $\text{PMe}(\text{p-C}_6\text{H}_4\text{Y})_2$] show that the trans/cis ratio is favored by (1) making L bulkier, (2) changing X^- from N_3^- to Cl^- to I^- , (3) making Y more electronegative, and (4) going to less polar solvents. Unfortunately the range of O is very limited.

$\text{MX}_2[\text{P}(\text{o-Tol})_3]_2$ complexes tend to favor the trans isomer on going from $\text{P}(\text{o-p-Tol})_3$ or $\text{P}(\text{o-m-Tol})_3$ to $\text{P}(\text{o-o-Tol})_3$, from Cl or Br to I , and from Pt to Pd.¹⁴⁴

The rates of cis-trans equilibration in MX_2L_2 complexes also depend on the size of L. The much slower rate of $\text{PdCl}_2[\text{PMe}_2(\text{o-Tol})_2]$ compared to $\text{PdCl}_2[\text{PMe}_2\text{Ph}]_2$ has been attributed to steric interference of a rate-determining associative reaction.¹⁴⁵ Catalysis by added phosphines is a general feature of these reactions. A decreasing efficiency in the order $\text{PMe}_2\text{Ph} \sim \text{PBu}_3 > \text{PMe}_2(\text{o-Tol})_2 > \text{PMe}(\text{o-Tol})_2 > \text{PPh}_3$ indicates that smaller ligands are better isomerization catalysts.

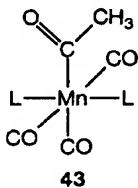
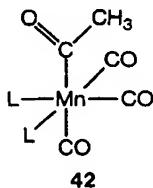
Selected trans/cis isomer ratios in $\text{CH}_3\text{COMn}(\text{CO})_4\text{L}$ complexes are shown in Table XLVII. $\text{P}(\text{OMe})_3$ has a greater tendency to go trans to the relatively bulky acyl than would be expected

TABLE XLVIII. Equilibrium Constants^a in Toluene-*d*₆ at 60 °C for the Reaction:

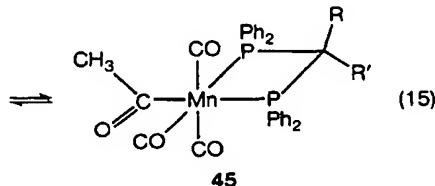
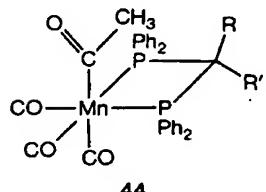
Carbene	L	K
M = Cr		
Me(OMe)C:	PM ₃	0.34
	PEt ₃	0.52
	PBu ₃	0.54
	P(octyl) ₃	0.56
	P(i-Pr) ₃	1.69
	PCy ₃	1.82
	P(<i>p</i> -Tol) ₃	0.19
	PPh ₃	0.22
	P(<i>p</i> -C ₆ H ₄ F) ₃	0.31
Me(OEt)C:	PBu ₃	0.50
Et(OMe)C:	PBu ₃	0.87
Ph(OMe)C:	PBu ₃	0.94
i-Pr(OMe)C:	PBu ₃	2.22
M = W		
Me(OMe)C:	PBu ₃	0.09
Ph(OMe)C:	PBu ₃	0.24

^a H. Fischer and E. O. Fischer, *Chem. Ber.*, **107**, 673 (1974).

on the basis of size alone. Reaction of *cis*-CH₃COMn(CO)₄L complexes with L gave only 42 at equilibrium when L = P(OCH₂)₃CMe or PHPh₂, a mixture of 42 and 43 when L = P(OMe)₃, and only 43 for the largest ligands PMe₂Ph, P(OPh)₃, PEt₃, or PMePh₂.¹⁴⁶ PPh₃ would not give a CH₃COMn(CO)₃L₂ complex.



Equilibrium 15 shifts toward 45 in the sequence R = R' = H < R = H, R' = CH₃ < R = R' = CH₃. With Ph₂PCH(CH₃)PPh₂, the only isomer observed is 46. If the CH₃CO is replaced by the smaller CH₃, only the fac isomer analogous to 44 is seen even if R = R' = CH₃.¹⁴⁷



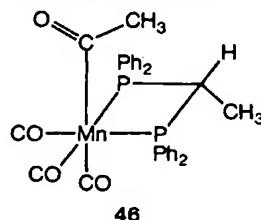
Trans/cis ratios in (carbene)M(CO)₄L complexes are larger for larger L, larger carbene, and smaller M (Table XLVIII). The aryl phosphine results are anomalous relative to the alkyl phosphines but do indicate a greater trans/cis ratio for more electronegative L.

Both electronic and steric factors are involved in the equi-

TABLE XLIX. Equilibrium Constants^a in CDCl₃ at 25 °C for the Reaction:

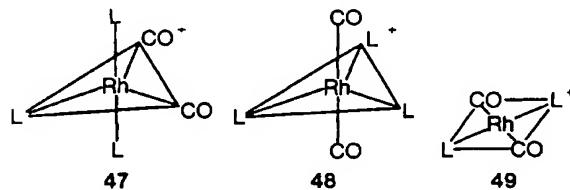
L	R = Cl		I		H		Me		Bz	
	Cl	Br	I	H	Me	Bz				
P(OPh) ₃	<0.02		<0.02	0.03	1.7	5.6				
SbPh ₃			0.04							
PBu ₃	<0.02		0.13	0.48	7.1					
PM ₃ Ph			0.36	0.93 ^b						
PPh ₃	<0.02	0.04	1.16	0.59 ^b	12.5 ^c	>50				
P(OMe) ₃	0.11	0.34	3.3	0.19	5.9					

^a J. W. Faller and A. S. Anderson, *J. Am. Chem. Soc.*, **92**, 5852 (1970). ^b in *o*-dichlorobenzene. ^c in toluene.



librium in Table XLIX. K does increase regularly in the sequences Cl < Br < I and H < Me < Bz.

While Rh(CO)₂L₃⁺ complexes have configuration 47 in solution (two carbonyl bands in the IR) when L = PMePh₂ or AsMePh₂, they have 48 when L = P(*p*-Tol)₃, PPh₃, AsPrPh₂, or AsPh₃.¹⁴⁸ Attempts to prepare a tris phosphine complex with P(*p*-Tol)₃ failed, giving only 49.



The isomer distribution in eq 16 (L = PR₃, AsR₃, or SbR₃) depends on both steric and electronic effects.¹⁴⁹ Equilibria shift to the right in the series R = Me < Et ~ Pr ~ Bu < *n*-pentyl < *n*-octyl < Isopentyl < *t*-Bu < *sec*-alkyl, SbR₃ < AsR₃ < PR₃, and X = CF₃ < Br < F ~ H < Me < OMe when L = AsEt₂(*p*-C₆H₄X). The more crowded isomers 50 and 51 or ones with two L's on the same Co were not seen.

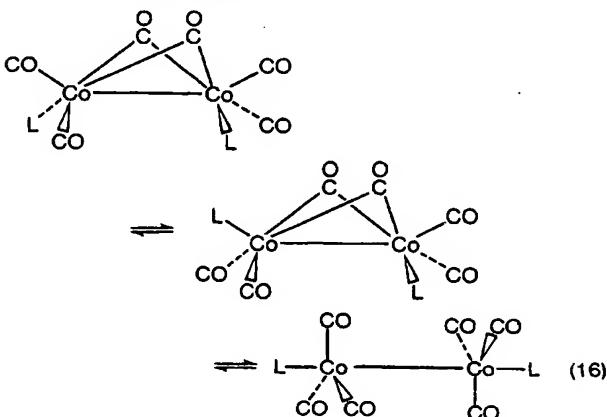
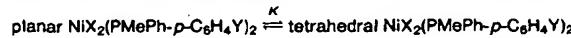


TABLE L. $\text{NiX}_2(\text{PR}_3)_2$ Isomers Isolated^a

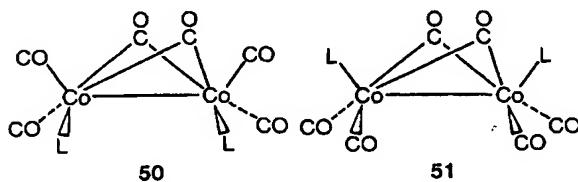
R	X = Cl	Br	I
Me	P	T	T
Et	P	P,T	T
Pr	P	P,T	T
Bu	P,T	P,T	T
n-Amyl	P,T	T	T
t-Bu	P	P,T	T
t-Pr	P	P,T	T,G
sec-Bu	P	P,T	T,G
t-Bu		T	T

^a From ref 151. Abbreviations: P, planar; T, tetrahedral; G, a green isomer of unknown structure.

TABLE LI. Equilibrium Constants^a in CDCl_3 at 25 °C for the Reaction:

Y	X = Cl	Br	I
CF ₃	0.15		0.56
Cl	0.23	0.75	1.22
H	0.41	1.43	2.70
Me	0.45	2.12	3.00
OMe	0.56	2.33	
NMe ₂	1.00	4.88	11.5

^a L. H. Pignolet, W. D. Horrocks, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, 92, 1855 (1970).



2. Square-Planar/Tetrahedral

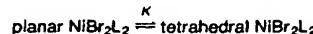
While PtX_2L_2 and PdX_2L_2 complexes usually form both cis and trans complexes, the planar complexes of the smaller cation $\text{Ni}(\text{II})$ are invariably trans; for certain X and L there can be an appreciable fraction of a paramagnetic tetrahedral isomer. For small R (e.g., Me or Et), $\text{NiX}_2(\text{PR}_3)_2$ and $\text{NiX}_2(\text{PR}_2\text{Ar})_2$ complexes are trans square planar and diamagnetic in the solid state and in solution. $\text{NiX}_2(\text{PAr}_2)_2$ complexes give a measurable amount of both isomers in solution while $\text{NiX}_2(\text{PAr}_3)_2$ are essentially 100% tetrahedral in both solution and solid states.¹⁵⁰

In the $\text{NiX}_2(\text{PRPh}_2)_2$ series, Hayter and Humiec¹⁵¹ were able to isolate the crystalline isomers shown in Table L. Both planar and tetrahedral isomers are present in the crystalline unit cell of $\text{NiBr}_2(\text{PPh}_2\text{Bz})_2$.¹⁵²

The tendency to favor the tetrahedral form in the sequence $\text{X} = \text{Cl} < \text{Br} < \text{I}$ is shown in the solid state in Table L and in solution in Table LI. The latter clearly shows the importance of electronic effects in the phosphine on K. The tetrahedral isomer is favored by electron-donating L. This is in accord with our observation, based on ESCA measurements,¹³⁹ that the $\text{Ni}(\text{II})$ in a tetrahedral isomer is more electron deficient than in the corresponding planar one. It cannot, however, explain the increase in K in the sequence $\text{PR}_3 < \text{PR}_2\text{Ph} < \text{PPh}_3$, which must therefore be determined primarily by steric effects.

Some results of a study by Que and Pignolet¹⁵³ are shown in Table LII. They concluded that steric effects are relatively unimportant. Their conclusion is, however, based on the questionable assumption that steric effects must be *monotonic* with increasing Θ .

Consider a *trans*- NiX_2L_2 complex 52 with small L. Increasing the size of L (or X) will cause a repulsive interaction between

TABLE LII. Equilibrium Constants^a in CH_2Cl_2 at 31 °C for the Reaction:

L	Θ	K	Ref
PM ₂ Ph ₂	136	1.78	153
PEt ₂ Ph ₂	140	2.03	155
PPr ₂ Ph ₂	140	2.33	155
PP ₃	145	b	153
PPh ₂ Cy	153	2.45	153
PPh ₂ Cy ₂	161	0.14	153
PCy ₃	170	0.00	153

^a From ref 153. ^b Very large.

L and X which can be relieved by a tetrahedral distortion toward 53, where the LNIX angles are opened from 90 to 109.5° (and



the LNIL angle is decreased from 180 to 109.5°). Still larger increases in Θ will lead to a severe repulsive interaction of L with L, favoring an opening of the LNIL angle back toward 52. The value of Θ for optimum stability of the tetrahedral form must be around 145°; PCy₃ is too large. A square-planar geometry for $\text{NiCl}_2(\text{PCy}_3)_2$ has been established by an x-ray study.¹⁵⁴

LaMar and Sherman¹⁵⁵ reported a second-order acceleration of the planar-tetrahedral interconversion for $\text{NiBr}_2(\text{PMePh}_2)_2$ with added phosphine, along with exchange of free and coordinated phosphine. PPh₃ exchanges more slowly with $\text{NiBr}_2(\text{PPh}_3)_2$. The still bulkier PPh₂Cy does not exchange with $\text{NiBr}_2(\text{PPh}_2\text{Cy})_2$ and its addition has no effect on the interconversion rate.¹⁵³

A steric effect is clearly shown in the planar-tetrahedral equilibrium of $\text{NiX}_2[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]$ complexes. Increasing n from 2 to 3 for X = Cl increases K from ~0 to 0.75 in CH_2Cl_2 at 22 °C.¹⁵⁶ An earlier study on the Br and I complexes gave a similar result.¹⁵⁷ Attempts to make $\text{NiX}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ complexes failed; the complexes isolated contained two monodentate diphosphines.

3. Ambidentate

Unsymmetrical diphosphines are capable of preferential bonding at one end. Reaction of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PMePh}$ with $(\text{C}_6\text{H}_5\text{NH}_2)\text{W}(\text{CO})_5$ in a 1:1 ratio gave predominantly (90%) the isomer with the -PMePh end coordinated. Reaction of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2(i\text{-Pr})$ gave predominantly (85%) the PPh₂ bound isomer.¹⁵⁸ The smaller end of the diphosphine is preferred in each case.

Reaction of $\text{P}(\text{OCH}_2)_2\text{P}$ with $(\text{C}_6\text{H}_5\text{NH}_2)\text{W}(\text{CO})_5$ in a 1:1 ratio at room temperature [or with $\text{Cr}(\text{CO})_6$ or $\text{Mo}(\text{CO})_6$ under UV radiation] gave predominantly the isomer with the smaller PO_3 end coordinated.¹⁵⁹ It was possible, however, to isolate both isomers by irradiation of $\text{Fe}(\text{CO})_5$,¹³ where the crowding is presumably less.

Changing the size of phosphorus ligands on a metal can affect the coordination of other ambidentate ligands, as we saw for SCN in Figure 12. Carty and co-workers¹⁶⁰ have concluded that steric effects also dominate the bonding mode in *trans*-Pd(SCN)₂L₂ complexes. The crystal structures show S bonding with L = P(OPh)₃ but N bonding with the larger PPh₃.

4. Other

An extremely important problem in many homogeneous catalytic reactions is how to control the formation of primary and

TABLE LVII. Barriers^a to Intramolecular Exchange in RhL_5^+ Complexes

L	ΔG^\ddagger , kcal/mol	T, K
$\text{P}(\text{OCH}_2)_3\text{CMe}$	7.8	153
$\text{P}(\text{OMe})_3$	7.5	200
$\text{P}(\text{OEt})_3$	9.9	208
$\text{P}(\text{OCH}_2)_3(\text{CH}_2)_3$	10.3	210
$\text{P}(\text{OBu})_3$	11.1	228

^a From ref 166.TABLE LVIII. ΔG^\ddagger (kcal/mol) in $\text{M}[\text{P}(\text{OCH}_2)_3\text{CMe}]_3$ Complexes^a

Co^+	10.0	Ni	8.3
Rh^+	7.8	Pd	5.7
Ir^+	8.4	Pt	7.0

^a P. Meakin and J. P. Jesson, *J. Am. Chem. Soc.*, **96**, 5751 (1974).TABLE LVIII. ΔG^\ddagger (kcal/mol) in HML_5 Complexes^a

$\text{HFe}(\text{PF}_3)_4^-$	<5	$\text{HCo}[\text{P}(\text{OCH}_2)_3\text{CPr}]_4$	
		$\text{HCo}[\text{P}(\text{OEt})_3]_4$	5.5
		$\text{HCo}[\text{P}(\text{OEt})_3]_4$	<6
		$\text{HRh}[\text{P}(\text{OCH}_2)_3\text{CPr}]_4$	10.5
$\text{HRu}(\text{PF}_3)_4^-$	7.0	$\text{HRh}(\text{PF}_3)_4$	9.0
		$\text{HRh}[\text{P}(\text{OEt})_3]_4$	7.25
		$\text{Hir}[\text{P}(\text{OCH}_2)_3\text{CPr}]_4$	10.3
$\text{HOs}(\text{PF}_3)_4^-$	8.0	$\text{Hir}(\text{PF}_3)_4$	10.0

^a P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Am. Chem. Soc.*, **94**, 5271 (1972), except for the $\text{P}(\text{OCH}_2)_3\text{CPr}$ complexes, by E. M. Hyde, J. R. Swain, J. G. Verkade, and P. Meakin, *J. Chem. Soc., Dalton Trans.*, 1169 (1976).

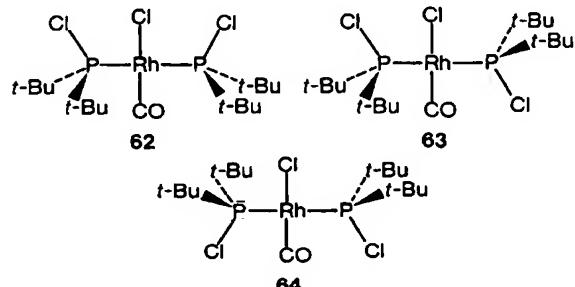
are consistent with the tetrahedral jump model; the heavy atoms need to move less if they are more nearly tetrahedral.

Rearrangement barriers in H_2ML_4 complexes ($\text{M} = \text{Fe}$ or Ru) do not change in a systematic way with steric or electronic changes in L.¹⁶⁷ The higher barriers for Ru (for example, 20.1 kcal/mol for $\text{H}_2\text{Ru}(\text{PMe}_2\text{Ph})_4$ vs. 13.9 for the Fe complex) are, however, consistent with the tetrahedral jump model. The unusual coupling constants observed in the iron complexes [$J_{\text{Pr}}(\text{cis}) > J_{\text{Pr}}(\text{trans})$] were attributed to their greater tetrahedral distortion.¹⁶⁷

Activation energies (in parentheses) for interconverting *cis*- and *trans*- $\text{HWCp}(\text{CO})_2\text{L}$ decrease as the size of L increases: PMe_3 (15.5 kcal/mol), PET_3 (14.7), PPh_3 (14.3).¹⁶⁸ On the other hand, the barrier is less for PPh_3 than for PCy_3 in $[\text{H}_2\text{Os}(\text{CO})(\text{NO})\text{L}_2]_2^+$.¹⁶⁹

Rotation of *t*-Bu groups on P can be frozen out at low temperature. Some measured activation energies include $\text{W}(\text{CO})_5\text{PPh}_2(\text{t-Bu})$ (8.3), $\text{P}(\text{t-Bu})_3$ (8.6), $\text{BH}_3(\text{t-Bu})_3$ (10.4), and $\text{SP}(\text{t-Bu})_3$ (10.5).¹⁷⁰

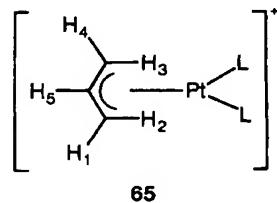
English and Bushweller have determined the first activation energy for rotation about a metal-phosphorus bond ($\Delta G^\ddagger = 12.6$ kcal/mol at -32°C) in *trans*- $\text{RhCl}(\text{CO})\text{PCl}(\text{t-Bu})_2$.¹⁷¹ The low-temperature limit $^{31}\text{P}\{^1\text{H}\}$ spectrum shows 62 (~90%), 63



(~10%), and 64 (~1%). The IR spectrum (cyclohexane) shows distinct ν_{CO} bands in decreasing intensity assignable to the three rotamers at 1996, 1975, and 1950 cm^{-1} . The decreasing stability along the series is consistent with the greater size of Cl ($\Theta = 102^\circ$) compared to CO ($\Theta = 92^\circ$).

Mann, Masters, Shaw, and Stainbank¹⁷² had earlier reported freezing out three rotamers of *trans*- $\text{RhCl}(\text{CO})[\text{PR}(\text{t-Bu})_2]_2$ ($\text{R} = \text{Me, Et, Pr}$) in the low-temperature ^{31}P NMR. Rotamers could not be frozen out with the smaller ligands PMe_2 , $\text{PMe}_2(\text{t-Bu})$, or $\text{PPr}_2(\text{t-Bu})$. Two rotamers can be seen in the 0°C ^1H NMR spectrum of *trans*- $\text{PdCl}_2[\text{PH}(\text{t-Bu})_2]_2$.¹⁷³

A nonequivalence of H_1 and H_4 at low temperature in 65 with $\text{L} = \text{PCy}_3$ has been attributed to restricted rotation about the Pt-P bond.¹⁷⁴ This behavior was not observed with the smaller $\text{L} = \text{PPh}_3$.

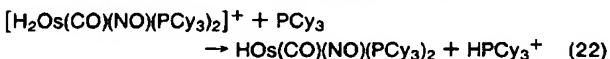
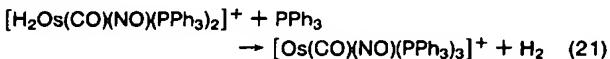


V. Unusual Reactions and Products

Changing the size of ligands frequently gives an unexpected reaction or unusual product. We have seen several examples in earlier sections. Here we are concerned primarily with products isolated from stoichiometric reactions. Section VI deals with catalytic reactions.

A. Displacement of Other Ligands

PPh_3 displaces H_2 in eq 21. The larger (and more basic) PCy_3 gives eq 22.¹⁷⁵

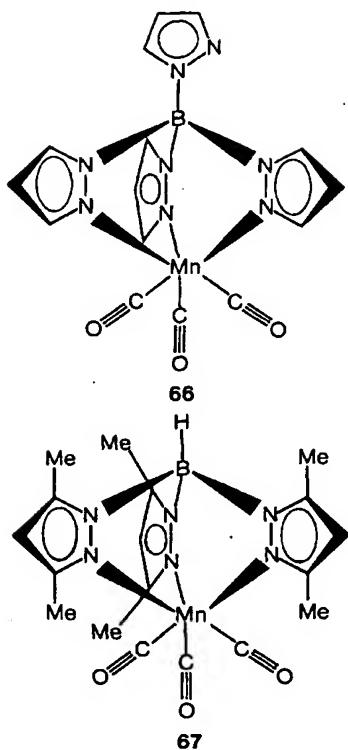


Reactions of various monodentate phosphorus ligands with $(\text{RC}\equiv\text{CR}')\text{Co}(\text{CO})_4$ (2:1 ratio in refluxing benzene) give disubstituted $(\text{RC}\equiv\text{CR}')\text{Co}(\text{CO})_2\text{L}_2$ complexes for $\text{L} = \text{P}(\text{OMe})_3$, PBU_3 , $\text{P}(\text{t-Bu})_3$, PPh_3 , $\text{PPH}_2(\text{sec-Bu})$, PPhC_3 , and PCy_3 . $\text{P}(\text{t-Pr})_3$, $\text{P}(\text{sec-Bu})_3$ and $\text{P}(\text{o-Tol})_3$ did not react at all, even in refluxing toluene. Under these conditions, excess $\text{P}(\text{OMe})_3$ gave tetrasubstituted $(\text{RC}\equiv\text{CR}')\text{Co}(\text{CO})_2\text{L}_4$.¹⁷⁶

Several years ago, King¹⁷⁷ tried to prepare $\text{M}(\text{CO})_3[\text{P}(\text{NMe}_2)_3]_3$ ($\text{M} = \text{Cr, Mo, W}$) by the reaction of the phosphine with (cycloheptatriene) $\text{M}(\text{CO})_3$. The reaction gave *trans*- $\text{M}(\text{CO})_4\text{L}_2$ instead. He attributed the failure to give trisubstitution to a special electronic effect (interaction of P with the N lone pairs). Actually $\text{P}(\text{NMe}_2)_3$ is very similar sterically (and electronically) to $\text{P}(\text{t-Pr})_3$. A similar failure to achieve trisubstitution has been found more recently for $\text{L} = \text{PCy}_3$ by Moers and Reuvers,¹⁷⁸ who also obtained only *trans*- $\text{M}(\text{CO})_4\text{L}_2$. In contrast, the smaller PMe_3 easily forms *cis*- $\text{M}(\text{CO})_4\text{L}_2$, $\text{M}(\text{CO})_3\text{L}_3$ and even $\text{M}(\text{CO})_2\text{L}_4$.¹⁷⁹

Schoenberg and Anderson¹⁸⁰ found that the degree of photochemical CO substitution on pyrazolylboratricarbonyl manganese(I) complexes 66 and 67 (Table LIX) decreases in increasing Θ , or on putting methyl groups on the pyrazolyl rings.

The maximum degree of substitution found for group 6B hexacarbonyls under UV irradiation is shown in Table LX. The largest ligand replaces only four CO's from the smallest metal.



B. Unusual Complexes of Arenes, Tetramethylethylene, CO_2 , N_2 , and Hydrides

Unusual complexes $(\text{arene})\text{Ni}[\text{Cy}_2\text{P}(\text{CH}_2)_n\text{PCy}_2]$ (arene = benzene, naphthalene, or anthracene; $n = 2$ or 3) and $(\text{naphthalene})\text{Ni}(\text{PCy}_3)_2$ can be prepared with very bulky ligands.¹⁸¹ Similar complexes of $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ or PMe_3 are unknown because of the stability of $\text{Ni}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2$ or $\text{Ni}(\text{PMe}_3)_4$.

The reaction of tetramethylethylene (TME) with $\text{Ni}(\text{Cy}_2\text{P}(\text{CH}_2)_2\text{PCy}_2)$ gives the olefin complex, whose x-ray crystal structure has been determined.¹⁸² The similar reaction of TME with the more crowded $\text{Ni}(\text{PCy}_3)_2$ does not go. Ethylene forms stable complexes in both cases.

Carbon dioxide complexes are still rare, presumably because of the weakness of bonding in most cases. The crystal structure of $(\text{CO}_2)\text{Ni}(\text{PCy}_3)_2$ has been reported.¹⁸³ The authors state that the stability of $(\text{CO}_2)\text{NiL}_2$ complexes depends on the basicity of L. It is clear, however, that steric effects are also very important.

The role of steric and electronic factors in the formation of $(\text{N}_2)\text{NiL}_3$ complexes was discussed in section IV.E. Green and Silverthorn¹⁸⁴ have similarly used a large, electron-donating phosphine to prepare $(\text{N}_2)\text{Mo}(\text{C}_6\text{H}_6)(\text{PMeCy}_2)_2$. Smaller ligands under the same conditions give $\text{Mo}(\text{C}_6\text{H}_6)\text{L}_3$ complexes.

While the reaction of phosphines with $[(\text{cyclooctene})_2\text{RhCl}]_2$ is a common method for preparing RhClL_3 complexes, a similar reaction of PCy_3 under nitrogen gives $(\text{N}_2)\text{RhCl}(\text{PCy}_3)_2$.¹⁸⁵

Unusual transition metal hydrides can be stabilized through steric effects. Thus, while HNIBrL_2 ¹⁸⁶ and HPdBrL_2 ¹⁸⁷ with $\text{L} = \text{PEt}_3$ decompose rapidly at room temperature, the corresponding complexes with $\text{L} = \text{P}(\text{i-Pr})_3$ or PCy_3 are stable and isolable.

Attempts to reduce $\text{trans-H}_2\text{PtCl}_2$ to $\text{trans-H}_2\text{PtL}_2$ leads to decomposition with small $\text{L} = \text{PMe}_2\text{Ph}$, PEt_3 , AsEt_3 , or PPh_3 . H_2PtL_2 compounds can, however, be prepared with $\text{PMe}_2(\text{i-Bu})$, $\text{PEt}_2(\text{i-Bu})$, $\text{PBu}_2(\text{i-Bu})$, $\text{PBz}_2(\text{i-Bu})$, $\text{PPr}(\text{i-Bu})_2$, $\text{PBz}(\text{i-Bu})_2$, and PCy_3 .¹⁸⁸ The more bulky the L, the more stable the complex. The crystal structure of $\text{trans-H}_2\text{Pt}(\text{PCy}_3)_2$ has been reported.²² An

TABLE LIX. Degree of Photochemical Substitution^a of Pyrazolylboratotricarbonylmanganese(I) Complexes

L	66	67
PF_3	1,2	1,2
$\text{P}(\text{OMe})_3$	1,2	1
$\text{P}(\text{OPh})_3$	1,2	1
PMe_3	1	1
PCl_3	1	0
PBu_3	1	1
PPh_3	1	0
$\text{P}(\text{i-Pr})_3$	1	0
PCy_3	1	0
$\text{P}(\text{C}_6\text{F}_5)_3$	0	0

^a From ref 180.

TABLE LX. Maximum Degree of Photochemical Substitution^a on $\text{M}(\text{CO})_6$

L	Cr	Mo	W
$\text{PF}_2(\text{OPr})$	6	6	6
$\text{PF}(\text{OMe})_2$	6	6	6
$\text{P}(\text{OMe})_3$	5	8	5
$\text{P}(\text{OMe})_2\text{Me}$	5	5	5
$\text{P}(\text{OMe})\text{Me}_2$	5	5	5
PMe_3	4	5	5

^a From ref 203.

earlier report¹⁸⁹ of the preparation of this and other H_2PtL_2 complexes by the AlR_3 reduction of $\text{Pt}(\text{acac})_2$ appears to be incorrect.¹⁸⁸

C. Unusual Coordination Numbers

With small L, the preferred coordination number for zerovalent Ni, Pd, and Pt is 4.^{2,9} This gives the metal an inert gas configuration of 18 electrons. ML_3 complexes can be isolated with PEt_3 ,^{83,119} $(\text{P}(\text{O}-\text{o-Tol})_3)$,¹⁹⁰ PPh_3 ,^{83,191} or PBz_3 .⁸³ Still larger ligands $\text{P}(\text{i-Pr})_3$,⁸³ PCy_3 ,^{23,83,192} $\text{PPh}(\text{i-Bu})_2$,⁸³ and $\text{P}(\text{i-Bu})_3$ ⁸⁵ can give 14-electron ML_2 complexes. X-ray structures have been reported for $\text{Pd}[\text{PPh}(\text{i-Bu})_2]_2$,^{65,193} $\text{Pd}(\text{PCy}_3)_2$,¹⁹³ and $\text{Pt}(\text{PCy}_3)_2$.²³

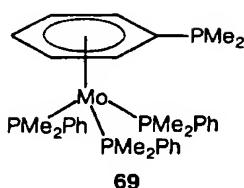
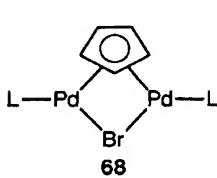
These ML_2 complexes appear to be the first structurally characterized exceptions to the 16- and 18-electron rule.¹²⁸

Unusual five-coordinate $\text{Pt}(\text{II})$ complexes PtX_2L_3 (X = Br, I) can be prepared with $\text{L} = \text{PMe}_2\text{Ph}$ but not with PEt_3 or PPh_3 .¹⁹⁴ CoBr_2L_3 complexes can be prepared when $\text{L} = \text{PPh}_2$ but not PPh_3 ; PMe_3 or PMe_2Ph but not PMePh_2 , PPh_3 , or PCy_3 .¹⁹⁵ $\text{Co}(\text{CN})_2\text{L}_3$ can be prepared when $\text{L} = \text{PPh}_2$ or PMePh_2 but not PPh_3 or PCy_3 .¹⁹⁵ While a number of ML_n^{n+} complexes are known with $\text{L} = \text{P}(\text{OCH}_2)_3\text{CMe}$, $\text{P}(\text{OMe})_3$, or $\text{P}(\text{OEt})_3$, none have been prepared with L as large as PMe_3 ($\Theta = 118^\circ$) or $\text{P}(\text{OPh})_3$ (128°).¹⁶⁶ $\text{Co}(\text{PMe}_3)_4^{+}$ does not react with PMe_3 to form a five-coordinate complex but does add PPhMe_2 ¹⁹⁶ to give $\text{Co}(\text{PMe}_3)_4(\text{PPhMe}_2)$.

Though $\text{Ir}(\text{III})$ complexes are usually six-coordinate (with 18 electrons), reactive 16-electron HirCl_2L_2 complexes can be prepared with $\text{L} = \text{PMe}(\text{i-Bu})_2$, $\text{PEt}(\text{i-Bu})_2$, and $\text{PPr}(\text{i-Bu})_2$.¹⁹⁷ Similarly, the unusual $\text{HMCi}(\text{CO})\text{L}_2$ complexes (M = Ru, Os) can be prepared when $\text{L} = \text{PCy}_3$.¹⁹⁸ A similar preparation with PPh_3 gives $\text{HMCi}(\text{CO})_3$.¹⁹⁹ NReCl_2L_n complexes form with $n = 3$ when $\text{L} = \text{PMe}_2\text{Ph}$, PEt_2Ph , PPr_2Ph , and PMePh_2 but $n = 2$ when $\text{L} = \text{PEtPh}_2$, PPrPh_2 , or PPh_3 .²⁰⁰

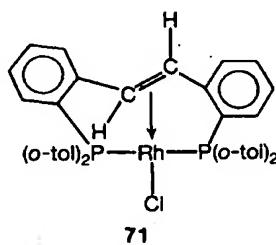
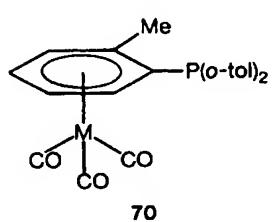
D. Products with Unusual Structures

A number of complexes of bulky phosphines have been found with novel structures or modes of bonding. A bridging cyclopentadienyl group occurs in 68 [$\text{L} = \text{PPh}_3$, $\text{P}(\text{i-Pr})_3$, or PCy_3]; the x-ray structure has been determined for $\text{L} = \text{P}(\text{i-Pr})_3$.²⁰¹



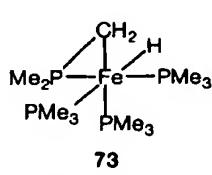
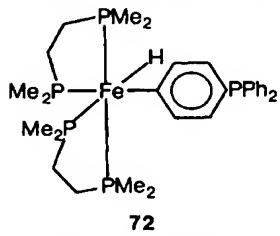
Though $\text{Mo}(\text{PF}_3)_6$ ²⁰² and $\text{Mo}[\text{P}(\text{OMe})_3]_6$ ²⁰³ are known, reduction of $\text{MoCl}_3(\text{THF})_3$ in the presence of excess PMe_2Ph gives " $\text{Mo}(\text{PMe}_2\text{Ph})_4$ "²⁰⁴ with structure 69. $\text{M}(\text{CO})_6$ -L₂ complexes (M = Cr, Mo or W) can be readily prepared from $\text{M}(\text{CO})_6$ with L = P(*p*-Tol)₃ or P(*m*-Tol)₃, but no disubstituted products are formed with P(*o*-Tol)₃. Attempts to force the reaction of $\text{M}(\text{CO})_6\text{P}(\text{o-Tol})_3$ with excess phosphine gave 70 instead.⁶³

Prolonged heating of RhCl_3 in 2-methoxyethanol with P(*p*-Tol)₃ or P(*m*-Tol)₃ gives the $\text{RhCl}(\text{CO})\text{L}_2$ complexes. With P(*o*-Tol)₃, 71 is obtained.²⁰⁶

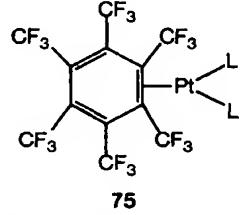
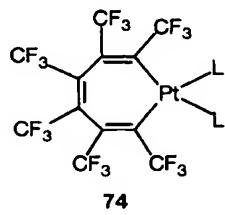


Reaction of $(\text{C}_{10}\text{H}_7)\text{FeH}(\text{dmpe})_2$ with $\text{P}(\text{OPh})_3$ or PEt_3 gives L $\text{Fe}(\text{dmpe})_2$ complexes (and C_{10}H_8). A similar reaction with PPh_3 gives 72.²⁰⁷

Reduction of Fe(II) salts in the presence of $\text{P}(\text{OMe})_3$ gives $\text{Fe}[\text{P}(\text{OMe})_3]_5$.²⁰⁸ A similar reaction with PMe_3 gives " $\text{Fe}(\text{PMe}_3)_4$ ", whose structure, by NMR, is 73.^{209,210}

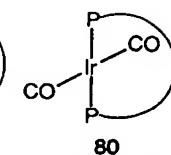
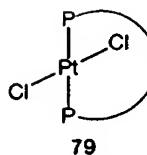
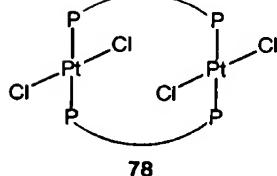
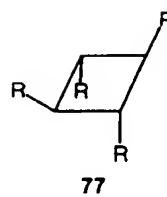
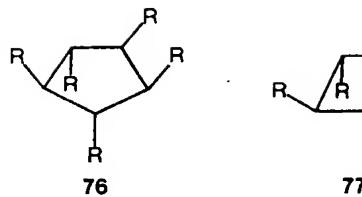


Hexakis(trifluoromethyl)benzene reacts with (*trans*-stilbene)PtL₂ with ring opening of the arene to give 74 with L = PMe₃. The reaction with L = PEt₃ gives 75 instead.²¹¹ Presumably 74 is too crowded to form with the larger phosphine.

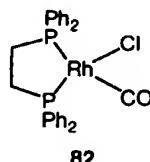
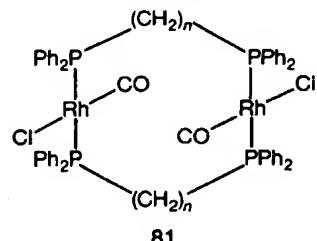


Cyclic polyphosphines (PR)_n form the five-membered ring 76 with R = Me, Et, Bu, or Ph but 77 with R = *i*-Pr, Cy, or *t*-Bu.²¹² Unfavorable steric crowding can be relieved by trans alternation of R groups in 77.

Unusual large ring compounds 78–80 can be formed using $(\text{t-Bu})_2\text{P}(\text{CH}_2)_{10}\text{P}(\text{t-Bu})_2$,²¹³ the bulky *t*-Bu groups prevent the phosphorus atoms from taking up mutually *cis* positions. A long chain is required to form mononuclear complexes. Thus, 79 could not be prepared with $(\text{t-Bu})_2\text{P}(\text{CH}_2)_5\text{P}(\text{t-Bu})_2$. Some x-ray structures have been reported.²¹⁴



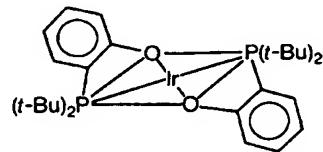
Reaction of $[\text{RhCl}(\text{CO})_2]_2$ with $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ gives 81 when n = 1, 3, or 4 but 82 when n = 2.²¹⁵



Attempts to prepare $\text{NiBr}_2[\text{P}(\text{t-Bu})_3]_2$ by the usual reaction of NiBr_2 with the phosphine²¹⁶ in alcohol gave instead $[\text{HP}(\text{t-Bu})_3]^+[\text{NiBr}_3\text{P}(\text{t-Bu})_3]^-$.²⁴

E. Unusual Oxidation States

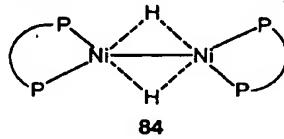
While the reaction of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with PEt_3 gives the RhCl_3L_3 complex,²¹⁷ similar reactions of PCy_3 ,²¹⁸ $\text{PEt}(\text{t-Bu})_2$,²¹⁹ or P(*o*-Tol)₃²⁰⁸ give the paramagnetic Rh(II) complexes RhCl_2L_2 . $\text{IrCl}_2(\text{PCy}_3)_2$ has also been prepared.²⁰⁶ The Ir(II) complex 83 has been prepared from IrCl_6^{3-} and $\text{P}(\text{t-Bu})_2(\text{o-C}_6\text{H}_4\text{OMe})$ and its x-ray structure determined.²²⁰ Note that the bulky P(*t*-Bu)₂ groups adopt mutually *trans* positions.



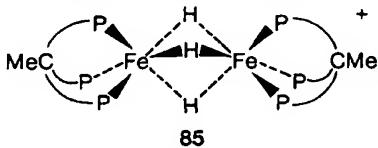
$\text{NiX}(\text{PPh}_3)_2$ ²²¹ (X = Cl, Br or I) and $[\text{NiX}(\text{PCy}_3)_2]$ ²²² (X = Cl or Br), both containing bulky L, are among the few examples reported of Ni(II) complexes containing monodentate phosphines.

Ni(II) complexes NiXp_3 [X = Cl or Br, $\text{p}_3 = \text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$] have been prepared from the reaction of NiX_2 with p_3 in the presence of NaBH_4 .²²³ NiI_2 reacts directly with p_3 to give NiIp_3 , whose x-ray structure has been determined.²²⁴ $\text{NiCl}(\text{Cy}_2\text{P-CH}_2\text{CH}_2\text{PCy}_2)$ and $\text{NiI}(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2)$ have also been reported.²²⁵

The nickel atoms in 84 are formally Ni(II), but the complex itself is diamagnetic; the diphosphine shown is $\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2$.



Using p_3 , Sacconi and co-workers²²⁶ have isolated a related complex, 85, and determined its crystal structure.

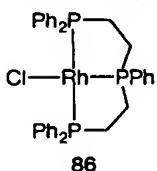


VI. Homogeneous Catalysis

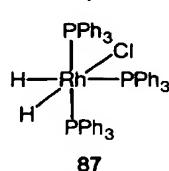
Over the past 20 years, the development of homogeneous catalysis has had a major impact on the growth of organometallic chemistry, much of which has been justified on the basis of the insight it gives into catalytic reactions. Several have proven practical for large-scale (over 100 million pounds per year) industrial syntheses of organic compounds. While our ability to design catalyst systems is still in its infancy, it is clear that phosphorus ligands are often involved and that their steric and electronic characters play extremely important roles. Learning to control catalytic reactions to give high yields of desired products under mild conditions will become increasingly important as the supply of petroleum for energy and feedstocks dwindles in the years ahead.

A. Reaction Rates

The rate of hydrogenation of cyclohexene by RhCl_3 catalysts increases in the sequence $\text{L} = \text{P}(p\text{-C}_6\text{H}_4\text{F}) \ll \text{PPh}_3 < \text{P}(p\text{-C}_6\text{H}_4\text{OCH}_3)$,²²⁷ indicating that electron donation by aryl phosphines increases activity, probably by increasing the rate and extent of oxidative addition by H_2 .²⁷ Replacing phenyl by ethyl, however, decreases the rate in the sequence $\text{PPh}_3 > \text{PEtPh}_2 > \text{PEt}_2\text{Ph} > \text{PEt}_3$.²²⁷ The difficulty here occurs at the next stage of the cycle, where L dissociation from the 18-electron H_2RhCl_3 is required before the olefin can coordinate.¹²⁸ The tripod phosphine complex 86 reacts readily with H_2 but is not a hydrogenation catalyst²²⁸ because the phosphorus atoms in the dihydride do not dissociate easily. Rapid dissociation of the PPh_3 trans to H in 87 has been demonstrated by NMR line-shape



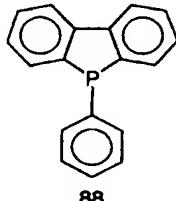
86



87

studies, but the $\text{H}_2\text{RhCl}(\text{PPh}_3)_2$ intermediate has not been detected spectroscopically.²⁷ H_2RhCl_2 complexes can, however, be isolated with bulky ligands²²⁹ like $\text{PMe}(t\text{-Bu})_2$, $\text{P}(t\text{-Bu})_3$,²³⁰ or PCys .¹⁸⁵ They are active hydrogenation catalysts.^{185,230}

A HRhL_4 catalyst an order of magnitude more active than $\text{HRh}(\text{PPh}_3)_4$ or $\text{RhCl}(\text{PPh}_3)_3$ for 1-hexene hydrogenation has been reported using $\text{L} = 5\text{-phenyl-5H-dibenzophosphole}$ (88). The enhanced activity was attributed to the rigid, bulky nature of the ligand.²³¹



88

The greater activity of 89 than 90 in olefin hydrogenation has been attributed to the more ready dissociation of an $\text{L} = \text{P}(\text{OPh})_3$ in the former.²³² Hydrogenation is inhibited in both cases by the addition of $\text{P}(\text{OPh})_3$.

TABLE LXI. Relative Hydrogenation Rates^a of Styrene by $\text{L} + [\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ ($\text{P}:\text{Rh} = 2.1:1$) in Benzene at Ambient Temperature and 1.1 atm of H_2

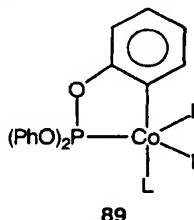
L	Rel rate	L	Rel rate
PPh_3	2.8	$\text{Ph}_2\text{P}(\text{CH}_2)_5\text{PPh}_2$	0.5
PEtPh_2	(1.00)	$\text{Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2$	0.22
$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$	0.5	cis- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$	0.07
$\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$	0.04	$\text{Ph}_2\text{PCH}_2\text{OCH}_2\text{PPh}_2$	0.03
$\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$	1.75	diop	0.17
$\text{Ph}_2\text{P}(\text{CH}_2)_5\text{PPh}_2$	0.25		

^a From ref 234.

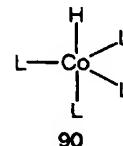
TABLE LXII. Hydroformylation of 1-Hexene at 160 °C and 1000 psig; $\text{H}_2:\text{CO} = 1.2:1$. Cobalt Carbonyl Catalyst

L	% ^a	L	% ^a
PBu_3	89.6	PEt_2Ph	84.6
PEt_3	89.6	PEtPh_2	71.7
PPr_3	89.5	PPh_3	62.4
$\text{P}(i\text{-Pr})_3$	85.0		

^a Linear aldehyde and alcohol. From ref 239.



89



90

Catalytic hydrogenation of benzene to cyclohexane is three times as fast with $\pi\text{-C}_3\text{H}_5\text{Co}[\text{P}(\text{OMe})_3]_2\text{P}(\text{O}-i\text{-Pr})_3$ as with $\pi\text{-C}_3\text{H}_5\text{Co}[\text{P}(\text{OMe})_3]_3$.²³³

The rate of styrene hydrogenation by rhodium catalysts containing $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ depends markedly on the value of n (Table LXI).²³⁴ Quite different relative rates are obtained if the substrate is changed to α -acetamidocinnamic acid.

The rate of addition of active hydrogen compounds to butadiene in a $\text{Ni}(\text{acac})_2/\text{P}(\text{OR})_2/\text{NaBH}_4$ system increases in the order $\text{R} = \text{Me} < \text{Et} < i\text{-Pr}$.²³⁵ Using preformed NiL_4 catalysts, only a trace of morpholine reacted in 1 h at 100 °C when $\text{L} = \text{P}(\text{OEt})_2\text{Ph}$, while 96% reaction was observed with $\text{P}(\text{O}-i\text{-Pr})_2\text{Ph}$.²³⁶

Both the rates and product distributions of butadiene cyclooligomerization with $\text{Ni}(0)/\text{L}$ catalysts depends on L .^{237a} The same is true in reactions involving added ethylene.^{237b}

B. Product Distributions

The major product of propylene dimerization in a $\pi\text{-C}_3\text{H}_5\text{Ni-LAICl}_3$ catalyst system changes from 2-methylpentenes to 2,3-dimethylbutenes on increasing the size of L in the series PMe_3 , PEt_3 , $\text{P}(i\text{-Pr})_3$.^{237c}

It has been known for some time that the addition of phosphines to the cobalt carbonyl catalyzed hydroformylation slows the reaction but gives a higher percentage of the desired linear aldehyde and alcohol products.²³⁸ Tucci²³⁹ observed the product distributions shown in Table LXII.

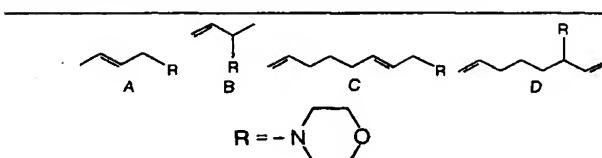
A more extensive study of $\text{HRh}(\text{CO})_{4-n}\text{L}_n$ catalyzed hydroformylation by Pruitt and Smith²⁴⁰ showed that both steric and electronic effects of L are important. Table LXIII shows that increased electron donation by para-substituted aryl phosphites decreases the percentage of linear aldehyde. A greater decrease is caused by making L more bulky. The role of ligand size can be understood by referring to Scheme I, where R^2 and R^1 refer to isomeric secondary and primary alkyls. Increasing the size of L should increase K_1 , K_2 , and K_3 . (Greater crowding in a

TABLE LXIII. Hydroformylation of 1-Octene at 90 °C and 80–100 psig, H₂:CO = 1:1; HRh(O)_{4-n}L_n Catalyst

L	% ^a	L	% ^a
P(O- <i>p</i> -C ₆ H ₄ Cl) ₃	93	P(OBu) ₃	81
P(OPh) ₃	86	P(O- <i>o</i> -Tol) ₃	78
P(O- <i>p</i> -C ₆ H ₄ Ph) ₃	85	P(O- <i>o</i> -C ₆ H ₄ Ph) ₃	52
P(O- <i>p</i> -C ₆ H ₄ OCH ₃) ₃	83	P[O-2,6-C ₆ H ₃ (Me) ₂]	47

^a Linear aldehyde. From ref 240.

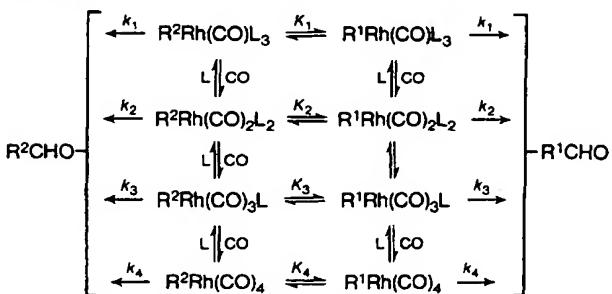
TABLE LXIV. Percentage of Products^a Produced for Morpholine and Butadiene with $\text{NiCl}_2/\text{L}/\text{NaBH}_4$ (1:2:1) at 20 °C In 6–9 h



L	A	B	C	D
$P(O-i-Pr)_3Ph$	13	77	8	1
$P(O-o-Tol)_3$	3	27	64	6
PPh_3	2	6	75	17
$P(O-o-C_6H_4Ph)_3$			85	15

^a R. Baker, A. Onions, R. J. Popplestone and T. N. Smith, *J. Chem. Soc., Perkin Trans. 2*, 1133 (1975).

SCHEME I



complex decreases the stability of a secondary alkyl more than a primary one.) But $K_1 > K_2 > K_3 > K_4$. Increasing the size of L improves the ability of CO to compete with L for coordination sites and increases the fraction of Rh present as $\text{RRh}(\text{CO})_3\text{L}$ and $\text{PRh}(\text{CO})_4$. In the limit of very large L, the product distribution will be that of a phosphine-free system.

Table LXIV shows the effect of changing L on the product distribution in the reaction of morpholine with butadiene. Larger L's compete less favorably with butadiene for coordination, allowing the butadiene to dimerize to a greater extent.

The trimers produced in the oligomerization of methylene-cyclopropane are markedly affected by the size of L, showing a smooth transition to cyclic products as the size of L increases (Table LXV). Apparently the hydride transfer step required to give open chain products becomes less favorable relative to carbon-carbon coupling.

Trost and Stregel²⁴¹ have shown that the position of attack of nucleophiles on 91 can be shifted to the primary carbon of the π -allyl by increasing the size of L. The result was explained in

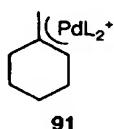
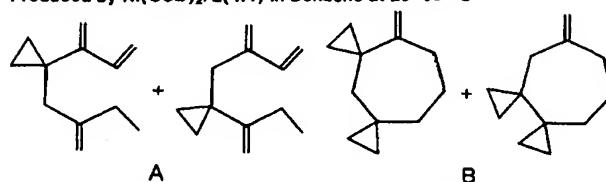


TABLE LXV. Percentage of Methyleneycyclopropane Trimers^a Produced by $\text{Ni}(\text{COD})_2/\text{L}$ (1:1) in Benzene at 25–60 °C



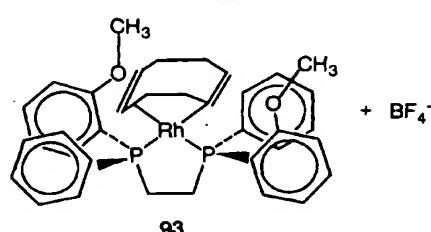
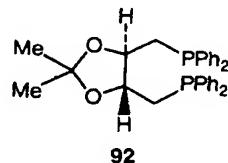
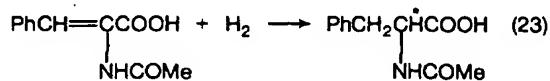
	% A	% B
PEt ₃ , ^b	92	2
PPh ₃	89	6
P(iPr) ₃	78	18
PCy ₃	72	23
P(i-Pr) ₂ (t-Bu)	18	69
P(t-Bu) ₃	0	80

^aP. Binger and J. McMeeking, *Angew. Chem., Int. Ed. Engl.* **12**, 995 (1973). ^bP. Binger, private communication.

terms of crowding in the (olefin)PdL₂ complexes which are the presumed primary products.

C. Asymmetric Induction

A discussion of steric effects on catalytic reactions would not be complete without mentioning the rapidly growing area of asymmetric induction. In 1968, Knowles and Sabacky²⁴² reported the first catalytic asymmetric hydrogenation, employing a Rh catalyst with the optically active ligand $(-)\text{PMePh}(\text{I-Pr})$. Later Dang and Kagan²⁴³ prepared the optically active amino acid *N*-acetylphenylalanine (eq 23) using a Rh catalyst containing the optically active diphosphine diop (92). Enantiomeric excesses of up to 96% have been achieved using 93 as the catalyst.²⁴⁴



Though Knowles and co-workers have argued that electrostatic interactions of the methoxy group with the substrate are involved in this case, it is clear that steric effects are very important and perhaps solely responsible for asymmetric induction in systems without methoxy substituents.²⁴⁵

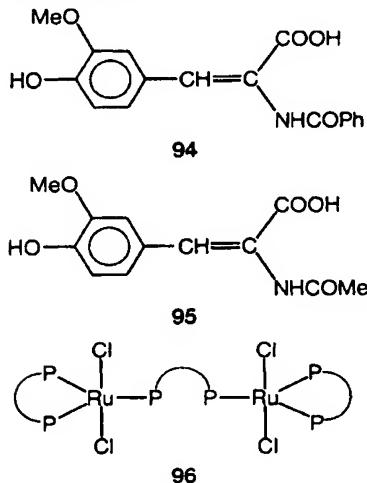
Table LXVI shows the effects of varying the structure of some optically active monodentate phosphines on the enantiomeric excess (L configuration) of α -amino acid produced by the hydrogenation of prochiral olefins 94 and 95 by $[(1,5\text{-cyclooctadiene})\text{RhL}_2]\text{BF}_4^-$.

A catalyst for asymmetric hydrogenation can be prepared from the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with (+)-diop to give 96.²⁴⁶ The reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ gives a coor-

TABLE LXVI. Enantiomeric Excess in Asymmetric Hydrogenation^a by $[(1,5\text{-COD})\text{RhL}_2]\text{BF}_4$ at 25 °C

L	Substrate	P_{H_2} (atm)	ee %
PMcPrPh	94	3.5	28
PMcPh(<i>o</i> -C ₆ H ₄ OMe)	94	3.5	58 ^b
PMcCy(<i>o</i> -C ₆ H ₄ OMe)	94	0.7	90
PMcBz(<i>o</i> -C ₆ H ₄ OMe)	95	3.5	47
PMc(<i>i</i> -Bu)(<i>o</i> -C ₆ H ₄ OMe)	95	3.5	49
PMc(<i>i</i> -Pr)(<i>o</i> -C ₆ H ₄ OMe)	95	3.5	85
PMcCy(<i>o</i> -C ₆ H ₄ OMe)	95	0.7	88
PMcCy(2-Me-4-BrC ₆ H ₃)	95	3.5	74

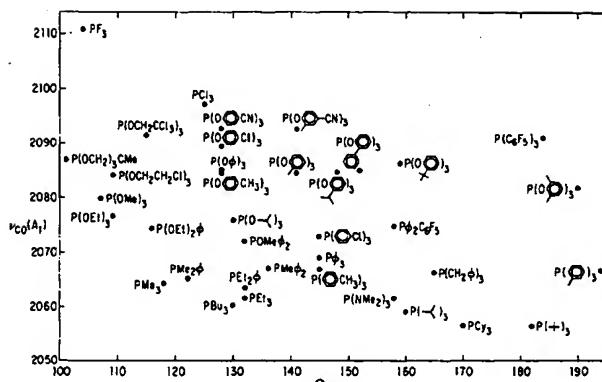
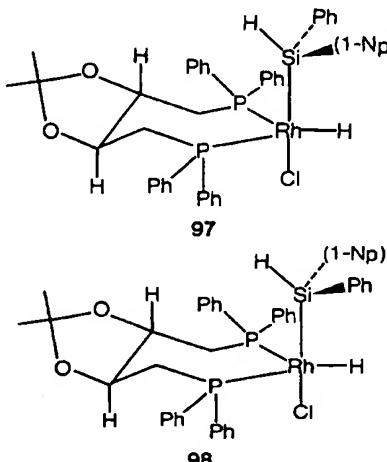
^a W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *Adv. Chem. Ser.*, No. 132, 274 (1974). ^b This run was by the anion procedure. The others were by the free acid procedure.



dinatively saturated complex $\text{RuCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$ which is inactive under similar conditions.

Asymmetric hydroformylation of olefins using optically active phosphines has been demonstrated.²⁴⁷ Though little work has been reported involving steric effects in the phosphines, it is clear that the size of substituents on the olefin is very important in controlling which face of the olefin preferentially coordinates.

Asymmetric hydrosilylation of carbonyl compounds has been used to prepare asymmetric alkoxy silanes (eq. 24).²⁴⁸ The preferred configuration of the product can be understood in terms of minimizing steric interactions in the intermediates; 97 is more stable than 98.



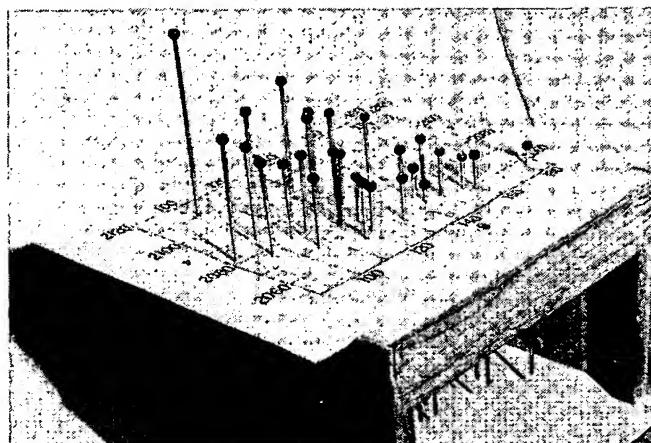


Figure 26. IP₁ of free phosphorus ligands in the gas phase. Data from references in Table XXVII. The height in inches is the number of electron volts above 7.0.

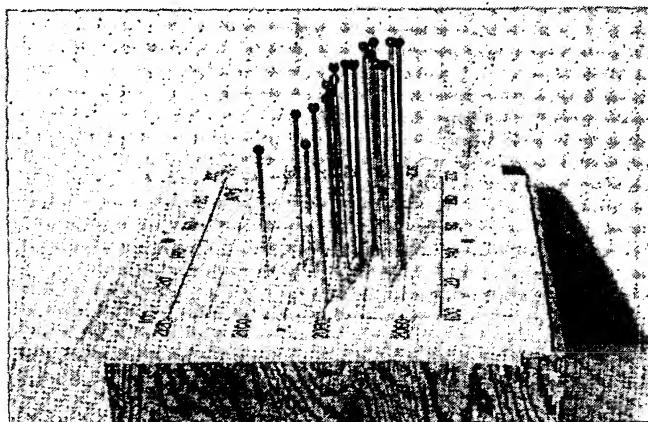
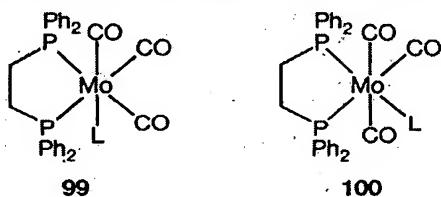


Figure 27. $\delta(^{13}\text{C})$ of the carbonyls in $\text{Ni}(\text{CO})_3\text{L}$ complexes, from ref 249b. The height in cm is the chemical shift (downfield from internal Me_4Si) in ppm beyond 180.

could, of course, depend on variables such as temperature, solvent, and ratios of reactants.

VIII. Steric Effects of Other Ligands

Though steric effects of ligands bonded by atoms other than phosphorus are strictly beyond the scope of this review, a few comments should be made. Other group 5 donors (ES_3) containing As, Sb, and Bi are expected to be slightly smaller than their P analogs. Models show that increasing M–E or E–C bond lengths by ~ 0.1 Å decreases cone angles by 3 to 5° . Pauling's tetrahedral covalent radii for P, As, Sb, and Bi are 1.10, 1.18, 1.36, and 1.46 Å.²⁵¹ Mean SES angles are also likely to be smaller for heavier group 5 donors. For example, the mean $CSbC$ angle of 101.8° in $Fe(CO)_4SbPh_3$ ²⁵² is 2.4° smaller than the CPC angle in $Fe(CO)_4PPh_2$.²⁵³ The Sb–Fe bond (2.47 Å) is 0.23 Å longer. The smaller size of $L = SbPh_3$ has been used to explain the formation of isomer **99** while $AsPh_3$ and PPh_3 form **100**.²⁵⁴



It should be borne in mind that, though carbonyl stretching frequencies in $M(CO)_n(ER_3)_m$ complexes are nearly independent

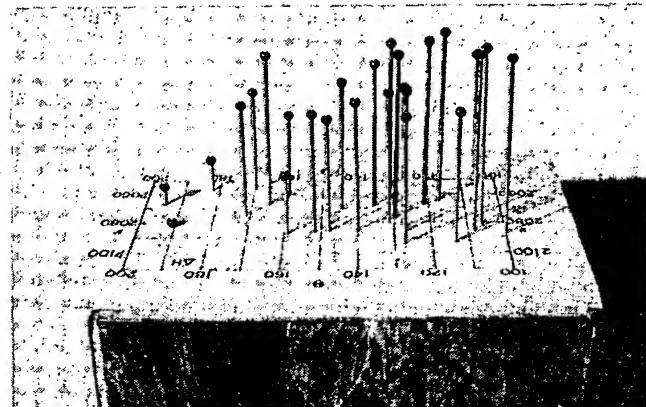
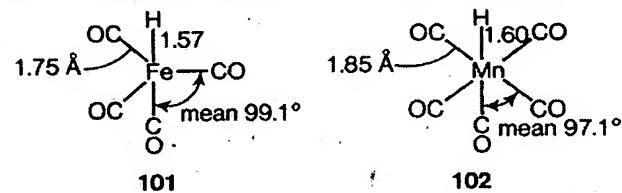


Figure 28. ΔH for reactions of *trans*-[MePt(PMe₂Ph)₂(THF)]PF₆ with excess L, from ref 250. The height in cm is one-half the number of kcal/mol.

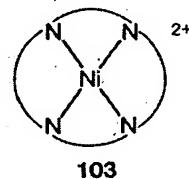
of E, the M–E bond strengths can be very different and generally fall rapidly in the order $P > As > Sb > Bi$.

Ligand cone angles can be defined for ligands other than those bonded by group 5 donor atoms. A few values for common types are given in Appendix C. The importance of steric effects in compounds not containing group 5 atoms is illustrated by the few following examples.

The structure of $\text{HFe}(\text{CO})_4^-$ (101)²⁵⁵ shows a greater bending of equatorial carbonyls toward the hydride than does $\text{HMn}(\text{CO})_5$ (102),²⁵⁶ whose metal has a larger covalent radius. A still greater deviation from idealized geometry is shown by $\text{HCo}(\text{PF}_3)_4$.²⁵⁷



The oxidation potentials of complexes 103 depend on the size of the macrocyclic tetraamine ring; increasing the ring size from 14 to 16 makes it more difficult to go from Ni(II) to Ni(III) by about 0.3 eV.²⁵⁸ Busch and co-workers have also shown that the fit



of the cation in the "hole" formed by the four N donors also affects the UV absorption spectrum.²⁵⁹ Increasing the M-N bond lengths beyond an optimum value (by increasing ring size) causes red shifts in the UV transitions, reminiscent of effects seen in section III.C. It is intriguing to note that the UV spectra of transition metal complexes can be changed by subjecting them to high pressures.²⁶⁰

Brintzinger²⁶¹ and co-workers have claimed that the insertion of WCp_2 into aromatic C-H bonds, not observed for the Cr and Mo analogues, is largely due to reduced steric crowding in the transition state of the larger metal.

The activation energy to bridge-terminal H interchange is much larger in $\text{Cp}_2\text{VH}_2\text{BH}_2$ than in $\text{Cp}_2\text{NbH}_2\text{BH}_2$. Marks and Kennelly^{262a} attribute this to the larger ionic radius of Nb. Significantly the $\text{Cp}_2\text{M}(\text{allyl})$ complex is η^1 for $\text{M} = \text{V}$ and η^3 for $\text{M} = \text{Nb}$.

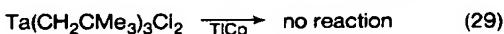
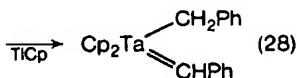
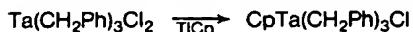
Formation of Schrock's alkylidene (eq 28) in the reduction of TaR_3Cl_2 complexes by thallium cyclopentadienide must de-

TABLE LXVII. Equilibrium Distribution^a of Products in the Reaction of HZrClCp₂ with RC≡CR'

R	R'	$\begin{array}{c} R \\ \\ R-C \equiv C-H \\ \\ (Zr) \end{array}$	$\begin{array}{c} R \\ \\ H-C \equiv C-(Zr) \\ \\ R' \end{array}$
H	Bu	>98	<2
Me	Et	89	11
Me	Pr	91	9
Me	i-Bu	>95	<5
Me	i-Pr	>98	<2
Me	r-Bu	>98	<2

^a D. W. Hart, T. F. Blackburn, and J. Schwartz, *J. Am. Chem. Soc.*, **97**, 679 (1975). ^b (Zr) = ZrClCp₂.

pend^{262b} on the conflicting steric requirements of the groups R and Cp, as seen in the following sequence of reactions:



Neopentyl groups are too large to permit even the first stage of reduction.

Addition of HZrClCp₂ to unsymmetrically disubstituted acetylenes gives a mixture of vinyl zirconium derivatives in which the steric bulk of the alkyl substituents on the acetylene determines the direction of addition (Table LXVII). The bulky ZrClCp₂ preferentially goes on the smaller end of the acetylene.

Collman's "picket fence porphyrin"²⁶³ (Figure 29) and Baldwin's "capped" porphyrin complex²⁶⁴ both utilize organic superstructure on the porphyrins to protect the Fe-coordinated O₂ in a manner analogous to the biological protein. The possibilities of modifying chemical behavior through changing molecular structure have hardly begun to be explored.

IX. Summary

Steric effects are extremely important to structures, spectroscopic properties, and chemical behavior of phosphorus ligands and their complexes. Increasing the size of substituents on P will tend to:

- open the SPS angles and the angles between L and other ligands on a metal;
- increase the bond lengths of M to P and to other ligands;
- reduce the s character in the phosphorus lone pair, thus decreasing $^1J_{MP}$ and shifting $\delta(^3P)$ to low field;
- increase the basicity of the lone pair;
- favor lower coordination numbers (possibly involving M-M bond cleavage);
- favor coordination of other ligands which are in competition for coordination sites;
- favor intramolecular oxidative addition reactions;
- favor isomers which are less crowded;
- increase the rates of dissociative reactions and decrease the rates of associative ones. If the L's become large enough, they can interfere with the coordination of other ligands which are normally strongly held, such as CO or O₂.

In order to reach conclusions about the relative importance of steric and electronic effects in a particular system, a wide range of ligand types should be used. The Steric and Electronic Map should be helpful, in conjunction with values of ν and θ from Appendixes A and B, and the additivity relationships.

It would be helpful to have cone angles from actual ligands

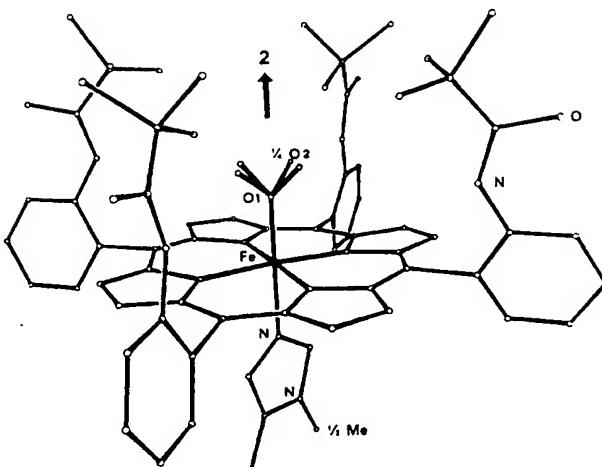


Figure 29. The O₂ complex of Collman's "picket fence porphyrin", showing the fourfold disorder in the O₂ position, from ref 263.

in x-ray crystal structures. Some efforts along these lines are underway in our and other²⁶⁵ laboratories. Hopefully someone in the near future will do the statistical analysis necessary to put the separation of phosphorus ligand steric and electronic effects on a sound mathematical basis. The idea of ligand cone angles should be extended to other types of ligands (such as those in Appendix C), and tested experimentally wherever possible. There is a great need at the present time for measurement of steric effects on heats of reaction. Calorimetric studies are in their infancy.²⁶⁶ Other areas in need of research are the role of steric effects in rates of reactions, electronic structure and spectra, and electrochemistry. The application of steric effects to the control of homogeneous catalytic reactions is probably the most important area and holds great promise for future research.

X. Addendum

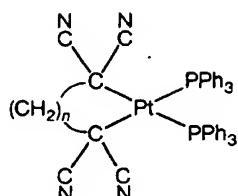
Since writing this review, a number of relevant articles have come to my attention. In particular, a review^{267a} on tertiary phosphine ligands by Mason and Meek discusses steric effects and independently arrives at a number of the conclusions presented here. A book entitled "The Chemistry of Phosphorus" by Emsley and Hall^{267b} has only a short section on steric effects but provides broad coverage for all sorts of phosphorus chemistry. For the convenience of the reader, I have listed the following additions in the order in which they would have appeared in the text, with an appropriate section number.

II. An x-ray crystal structure shows that trimesitylphosphine (mesityl = 2,4,6-trimethylphenyl) has a mean C-P-C angle of 109.7°,^{268a} the largest value reported for a free phosphine. Trimesitylmethane, with a smaller central atom, has an even larger (C-C-C) angle of 115.9°.^{268b} CPK models show that P(mesityl)₃ has a ligand cone angle of 212°. The ³¹P chemical shift has an unusual value of +36.6 ppm, and the DS (Figure 9) is 0.^{268c}

The x-ray crystal structure of Mo(CO)₅[P(CH₂)₃(NCH₂)₃] has been solved to give a ligand cone angle of 102 ± 0.5° for the symmetric phosphine cage.²⁶⁹

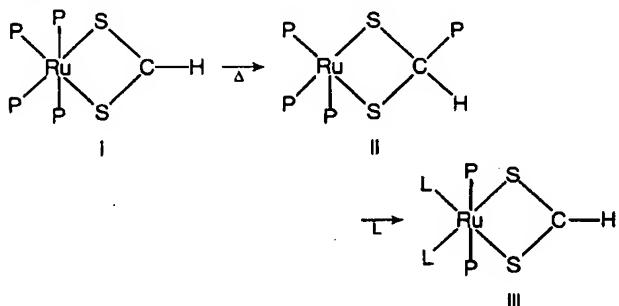
X-ray studies of CuCl(PPh₃)₃ and CuCl(PMePh₂)₃ have been determined and compared, and the role of steric effects on the structures of 31 phosphine or arsine complexes of Cu(I) summarized.²⁷⁰

Graziani and co-workers²⁷¹ have found that increasing the size of the methylene chain ($n = 0, 1$, and 2) in complexes of the type

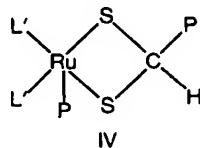


decreases the P-Pt-P angle from 101 to 93° and increases the Pt-P bond length from 2.29 to 2.33 Å.

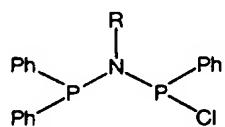
The orange dithioformate complex $\text{Ru}(\text{S}_2\text{CH})(\text{PMe}_2\text{Ph})_4^+$ (I) isomerizes on heating to a purple complex (II) in which a bulky axial phosphine (P) has been pushed from Ru to C.²⁷² Substituting the equatorial phosphines by the smaller L = P(OMe)₃ causes the axial phosphine to move back to Ru, giving the yellow



complex III. Treatment of II with the larger $L' = P(OMe)_2Ph$ gives only the purple C-bonded IV.



III.A. Values of $J(\text{PNP})$ in

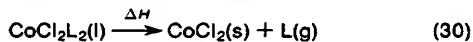


depend markedly on the size of R as follows: R = Me (+334), Et (+158), *t*-Pr (-29), and *t*-Bu (-35).²⁷³

III.B. Verkade and co-workers²⁷⁴ have shown that NO stretching frequencies in $\text{NO}(\text{NIL}_3)^+$ complexes (where L is an acyclic, cyclic, or bicyclic phosphite) increase as the molecular constraint is increased. They find a good correlation between ν_{NO} and $^1J_{\text{PH}}$ in the corresponding HL^+ .

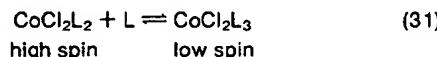
III.C. UV spectra of *trans*-IrCl(CO)L₂ complexes show shifts to shorter wavelength as the size of L increases.²⁷⁵ Values for the longest wavelength band (in C₆H₆) are: P(*p*-Tol)₃ (440), PPh₃ (439), PCy₃ (430), P(*o*-Tol)₃ (418 nm).

IV.A. A thermochemical study²⁷⁸ of CoCl_2L_2 complexes by differential thermal analysis indicates that more strongly electron-accepting phosphines tend to have stronger P-Co bonds; however, steric bulk weakens the bonds. Thus in eq 30 $\text{L} = \text{P}(\text{i-Pr})_3$ requires about 16 kcal/mol less than $\text{L} = \text{PEt}_3$.



A study²⁷⁷ of eq 31 by an accurate NMR susceptibility method [$L = P(OEt)_3$, $P(OEt)_2Et$, $P(OEt)Et_2$, or PEt_3] has shown that K depends on both electronic and steric effects; the middle members of the series give the most stable five-coordinate

complexes. A similar result was obtained in a study of $\text{Ni}(\text{CN})_2[\text{P}(\text{OMe})_3\text{Me}_3-n]_2$ complexes.²⁷⁸



IV.D. A kinetic study of the reaction of *N*-methylaniline with *cis*-PdCl(CN-*p*-C₆H₄Me)(L) complexes to give carbene complexes (by attack of the amine on the isocyanide carbon) shows that the rates depend on both steric and electronic properties of L.²⁷⁹ The reaction is favored by small L's which are good electron acceptors.

IV.E. Steric factors control the ligand exchange equilibrium observed when $(\text{o-Tol})\text{NiBr}(\text{PPh}_3)_2$ is treated with other phosphorus ligands, as shown by ^{31}P NMR studies.²⁸⁰

phosphine ligands, as shown by ^{1}H and ^{31}P NMR studies. IV.G. Anderson and co-workers²⁸¹ have shown by ^{1}H and ^{195}Pt INDO R measurements on solutions of *trans*-Pt(CNS)₂[As-Me₃-_nEt₂]₂ complexes that the coordination mode of the thiocyanate ligands is sensitive to the size of the arsines. As n increases from 0 to 3, the distribution changes from 69 % S,S to 83 % N,N bonded. The ^{195}Pt chemical shift is diagnostic for the coordination mode.

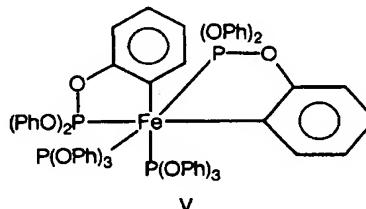
V. While most trialkylphosphines, including PEt_3 and PCy_3 , form adducts with CS_2 , $\text{P}(t\text{-Bu})_3$ does not.²⁸² This further emphasizes that PCy_3 acts smaller than $\text{P}(t\text{-Bu})_3$. While most trialkyl phosphites react readily with diethyl peroxide to form pentoxy phosphoranes,²⁸³ $\text{P}(\text{O}-t\text{-Bu})_3$ does not react under the same conditions.²⁸⁴

V.B. The very bulky ligands $\text{PPh}(\text{t-Bu})_2$ and $\text{P}(\text{t-Bu})_3$ react with H_3IrCl_6 to give the dihydrides H_2IrClL_2 , while the less bulky ligands $\text{PMe}(\text{t-Bu})_2$ and $\text{PEt}(\text{t-Bu})_2$ give the monohydrides HlrCl_2L_2 .²⁸⁵ The authors propose that the larger ligands favor H over Cl because a hydride ligand causes less steric strain.

V.C. Otsuka and co-workers²⁸⁶ have published the details of the preparations and x-ray structures of their PdL_2 and PtL_2 -complexes [$L = P(t\text{-Bu})_3, PPh(t\text{-Bu})_2, PCy_3$ and $P(i\text{-Pr})_3$]. $P(i\text{-Pr})_3$ is small enough to allow isolation of $Pt[P(i\text{-Pr})_3]_3$, from which one ligand can be readily removed. The still smaller $P(O\text{-}o\text{-Tol})_3$ gives only a three-coordinate Pt complex. $P(t\text{-Bu})_3$ is so large that even the small molecule O_2 does not react with $Pd[P(t\text{-Bu})_3]_2$.⁶⁵ The authors do, however, define cone angles incorrectly.²⁸⁶

V.D. An unusual *cis* dihydride of platinum, $\text{H}_2\text{Pt}\{o-[(t\text{-Bu})_2\text{PCH}_2]_2\text{C}_6\text{H}_4\}$, has been prepared with a bulky chelating diphosphine. It fails to react with HCl even on prolonged treatment.²⁸⁷

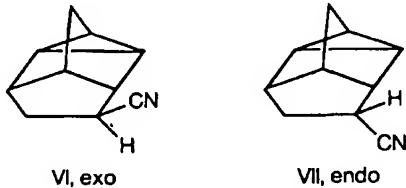
We have been able to make the five-coordinate $\text{Fe}(0)$ complex $\text{Fe}[\text{P}(\text{OCH}_2)_3\text{CET}]_5$ by treatment of $\text{Fe}(\text{COD})_2$ [$\text{COD} = 1,5\text{-cy-clooctadiene}$] with the phosphite.²⁸⁸ A similar reaction with the bulkier $\text{P}(\text{OPh})_3$ gives a product analyzing for " $\text{Fe}[\text{P}(\text{OPh})_3]_4$ " whose spectroscopic properties and reactions show it to be V^{289} . Ligands of intermediate size $[\text{P}(\text{OMe})_3, \text{P}(\text{OEt})_3$ and $\text{P}(\text{O-i-Pr})_3]$ give $(1,3\text{-COD})\text{FeL}_3$ complexes.²⁹⁰



Irradiation of solutions of $\text{Fe}(\text{CO})_5$ in the presence of $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1, 2, 3$, or 4) gave $\text{Fe}(\text{CO})_4\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\text{Fe}(\text{CO})_4$. In the case of $n = 1$ only, however, three other products were formed: $\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{Fe}(\text{CO})_4$, $\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{Fe}(\text{CO})_3$, and $\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{Fe}_2(\text{CO})_7$.²¹ We have found that reactions of excess $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ with $(\text{COD})_2\text{NI}$

give $\text{Ni}[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]_2$ for $n = 2, 3$, or 4 but for $n = 1$ give $(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{Ni}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$ in which two ligands are monodentate and one is bidentate.¹¹⁶

VI.B. Yoshikawa and co-workers²⁹² have shown that phosphorus ligand steric effects dominate the product distribution in the nickel catalyzed 4 + 2 cycloaddition of norbornadiene to acrylonitrile, giving VI and VII. Larger ligands favor VII. In the 2 + 2 cyclodimerization of norbornadiene, on the other hand, electronic factors dominate.²⁹³



Heimbach and co-workers²⁹⁴ are using the idea of the Steric and Electronic Map to fit data on product distributions in a variety of homogeneous catalytic reactions. By expressing the surfaces as polynomial expansions in ν and Θ and optimizing the coeffi-

cients by least squares, they are able to specify the percentage of electronic and steric control in each reaction.

VIII. $\text{Et}_2\text{Pt}(\text{PPh}_3)_2$ is much less stable than the metallocycle $(\text{CH}_2)_4\text{Pt}(\text{PPh}_3)_2$. This difference can be rationalized in terms of the steric constraints of the ring, which prevent the 0° Pt-C-H dihedral angle necessary for β -hydride elimination.²⁹⁵ The more flexible $(\text{CH}_2)_6\text{Pt}(\text{PPh}_3)_2$ complex is only marginally more stable than the dimethyl.

The isolation of $\text{M}[\text{SbAr}_3]_4$ complexes ($\text{M} = \text{Ni}, \text{Pd}, \text{or Pt}; \text{Ar} = \text{Ph}$ or para-substituted phenyl) which do not dissociate extensively in solution²⁹⁶ indicates that SbAr_3 ligands have smaller effective cone angles than the corresponding PAr_3 , whose ML_4 complexes are completely dissociated in solution at ambient temperature.⁵⁸

A study of the coordination mode of BH_4^- in the series $\text{Cp}_2\text{LnBH}_4\text{THF}$ (Ln = lanthanide element) shows that decreasing the effective ionic radius from 1.09 \AA (samarium) to 0.98 \AA (ytterbium) causes the BH_4^- to go from tridentate to bidentate.²⁹⁷

Kinetically stable MR_2 ($\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$) complexes have been prepared using the very bulky $\text{R} = \text{CH}(\text{SiMe}_3)_2$ or $\text{N}(\text{SiMe}_3)_2$.²⁹⁸

XI. Appendixes

APPENDIX A. Values^a of the Electronic Parameter ν

Type of Phosphorus Ligand				
PX_3	$\text{P}(\text{OR})_3$	PR_3	Other	ν, cm^{-1}
$\text{P}(\text{NMe}_2)_3$		$\text{P}(\text{i-Bu})_3$		2058.1
		PCy_3		2058.4
		$\text{P}(\text{o-C}_6\text{H}_4\text{OMe})_3$		2058.3
		$\text{P}(\text{i-Pr})_3$		2059.2
		PBu_3		2060.3
		PEt_3		2061.7
				2061.9 ^b
		PEt_2Ph		2063.7
		$\text{PPh}(\text{pip})_2$		2064.0
		PMe_3		2064.1
		$\text{P}(\text{p-C}_6\text{H}_4\text{OMe})_3$		2065.3
		PBz_3		2066.1
		$\text{P}(\text{o-Tol})_3$		2066.4 ^b
		$\text{P}(\text{p-Tol})_3$		2066.6
		$\text{P}(\text{m-Tol})_2$		2066.7
			PEtPh_2	2067.0
			$\text{PMePh}_2, \text{PPh}_2\text{pip}$	2067.2
			PPh_2NMe_2	2067.3 ^b
			$\text{PPh}_2(2,4,6\text{-C}_6\text{H}_2\text{Me}_3)$	2067.4
			PPh_2Bz_2	2067.6
			$\text{PPh}_2(\text{p-C}_6\text{H}_4\text{OMe})$	2068.2
			PPh_2Bz	2068.4
		PPh_3		2068.9
			$\text{PPh}_2(\text{CH}=\text{CH}_2)$	2069.3
		$\text{P}(\text{CH}=\text{CH}_2)_3$	$\text{PPh}_2(\text{p-C}_6\text{H}_4\text{F})$	2069.5
			$\text{PPh}_2(\text{m-C}_6\text{H}_4\text{F})$	2070.0
			$\text{PPh}_2\text{CH}_2\text{CH}_2\text{Cl}$	2070.8 ^b
		$\text{P}(\text{p-C}_6\text{H}_4\text{F})_3$		2071.3
			$\text{P}(\text{OEt})\text{Ph}_2$	2071.6
			$\text{P}(\text{OMe})\text{Ph}_2$	2072.0
			$\text{P}(\text{O-i-Pr})_2\text{Ph}$	2072.2
		$\text{P}(\text{p-C}_6\text{H}_4\text{Cl})_3$		2072.8
			$\text{P}(\text{Ph})\text{Ph}_2$	2073.3
			$\text{P}(\text{OBu})_2\text{Ph}$	2073.4
		$\text{P}(\text{m-C}_6\text{H}_4\text{F})_3$		2074.1
			$\text{P}(\text{OEt})_2\text{Ph}$	2074.2
			$\text{P}(\text{OPh})\text{Ph}_2$	2074.6
			$\text{PPh}_2\text{C}_6\text{F}_5$	2074.8
			$\text{PPh}_2(\text{o-C}_6\text{H}_4\text{Cl})$	2075.9
			PH_2Ph	2076.1
				2076.3
				2077.0

Appendix A (Continued)

Type of Phosphorus Ligand				
PX ₃	P(OR) ₃	PR ₃	Other	ν, cm^{-1}
		P(CH ₂ CH ₂ CN) ₃		2077.9
			P(OCH ₂) ₂ Ph	2078.7
	P(OCH ₂ CH ₂ OMe) ₃			2079.3
	P(OMe) ₃			2079.5
			P(OPh) ₂ Ph	2079.8
			PClPh ₂	2080.7
			PM ₂ CF ₃	2080.9
PH ₃	P(O-2,4-C ₆ H ₃ Me ₂) ₃			2083.2 ^c
	P(OCH ₂ CH ₂ Cl) ₃			2084.0
	P(O-p-Tol) ₃ , P(O-p-C ₆ H ₄ OMe) ₃			2084.1
	P(O-o-Tol) ₃			2084.6 ^b
	P(O-o-C ₆ H ₄ -i-Pr) ₃			2085.0 ^b
	P(O-o-C ₆ H ₄ Ph) ₃			2085.3
	P(OPh) ₃			2086.1 ^b
	P(O-o-C ₆ H ₄ -t-Bu) ₃			2086.5
	P(OCH ₂) ₃ CPr, P(OCH ₂) ₃ CEt		P(OCH ₂) ₂ OPh	2086.8
	P(OCH ₂) ₃ CMe			2087.3
	P(OCH ₂ CH ₂ CN) ₃			2087.6
	P(O-o-Tol-p-Cl) ₃			2088.2
	P(O-p-C ₆ H ₄ Cl) ₃			2089.3
		P(C ₆ F ₅) ₃		2090.9
	P(OCH ₂ CCl ₃) ₃		PCl ₂ Ph	2091.7
	P(O-p-C ₆ H ₄ CN) ₃			2092.1
PCl ₃				2092.8
PF ₃				2097.0
				2110.8

$$\text{Substituent Contributions to } \nu \text{ for } \text{PX}_3\text{X}_2\text{X}_3: \nu = 2056.1 + \sum_{i=1}^3 X_i$$

Substituent X _i	X _i	Substituent X _i	X _i
t-Bu	0.0	p-C ₆ H ₄ OMe	3.4
Cy	0.1	o-Tol, p-Tol, Bz	3.5
o-C ₆ H ₄ OMe	0.9	m-Tol	3.7
i-Pr	1.0	Ph	4.3
t-Bu	1.2 est	CH=CH ₂	4.5
Bu	1.4	p-C ₆ H ₄ F	5.0
Et	1.8	p-C ₆ H ₄ Cl	5.6
NMe ₂	1.9	m-C ₆ H ₄ F	6.0
piperidyl	2.0	CH ₂ CH ₂ Cl	6.1 ^b
Me	2.6	O-i-Pr	6.3
2,4,6-C ₆ H ₂ Me ₃	2.7	OBu	6.5
OEt	6.8	(OCH ₂) ₂ /2	9.8
CH ₂ CH ₂ CN	7.3	O-o-C ₆ H ₄ -t-Bu	10.0 ^b
OMe, OCH ₂ CH=CH ₂ , OCH ₂ CH ₂ OMe	7.7	OCH ₂ CH ₂ CN	10.5
H	8.3	O-o-Tol-p-Cl	11.1
O-2,4-C ₆ H ₃ Me ₂	9.0	C ₆ F ₅	11.2
OCH ₂ CH ₂ Cl, O-o-Tol, O-p-Tol, O-p-C ₆ H ₄ OMe	9.3	O-o-C ₆ H ₄ Cl	11.4
O-o-C ₆ H ₄ -i-Pr	9.5 ^b	OCH ₂ CCl ₃	11.9
O-o-C ₆ H ₄ -t-Bu	9.6 ^b	O-p-C ₆ H ₄ CN	12.2
OPh	9.7	Cl	14.8

^a $\nu_{CO}(A_1)$ of $\text{Ni}(\text{CO})_4\text{L}$ in CH_2Cl_2 from ref 1 unless noted otherwise. pip = piperidine. ^b Previously unpublished value. ^c This value for PH₃ was estimated from extrapolation of values for PH_{3-n}Ph_n ($n = 1$ to 3).

APPENDIX B. Values^a of the Ligand Cone Angle Θ

Type of Phosphorus Ligand				
PX ₃	P(OR) ₃	PR ₃	Other	Θ, deg
PH ₃	P(OCH ₂) ₃ CR'		PH ₂ Ph ^{b,c}	87
PF ₃	P(OCH ₂) ₃ (CH ₂) ₃			101
	P(OMe) ₃			104
			Me ₂ PCH ₂ CH ₂ PM ₂	106
				107

APPENDIX B (Continued)

Type of Phosphorus Ligand				
PX ₃	P(OR) ₃	PR ₃	Other	θ, deg
P(NCH ₂ CH ₂) ₃	P(OEt) ₃			108
	P(OCH ₂ CH ₂ Cl) ₃			109
	P(OCH ₂ CCl ₂) ₃ ^o	P(CH ₂ O) ₃ CR ^b	Et ₂ PCH ₂ CH ₂ PEt ₂ ^{b,d}	110
			P(OMe) ₂ Ph, P(OMe) ₂ Et	114
			P(OEt) ₂ Ph ^{b,c}	115
		PM ₃		116
				118
			Ph ₂ PCH ₂ PPh ₂ ^{b,d}	121
PCl ₃			PM ₂ Ph ^{b,c}	122
			PM ₂ CF ₃ ^b	124
			Ph ₂ PCH ₂ CH ₂ PPh ₂ ^{b,d}	125
			Ph ₂ P(CH ₂) ₃ PPh ₂ ^{b,d}	127
			PHPPh ₂ ^b	128
PBr ₃	P(OPh) ₃ , P(O- <i>p</i> -Tol) ₃ ^f			130
	P(O- <i>i</i> -Pr) ₃ ^f			131
		PEt ₃ , PBu ₃ , ^g PPr ₃ , ^h	POMePh ₂ ^f	132
		P(CH ₂ CH ₂ CN) ₃	POEtPh ₂ ^b	133
			PM ₂ Ph ₂ , ⁱ PEt ₂ Ph ^b	136
		P(CF ₃) ₃		137
			PEtPh ₂ ^b	140
	P(O- <i>o</i> -Tol) ₃ ^f		Cy ₂ PCH ₂ CH ₂ PCy ₂ ^{b,d}	141
				142
		P(<i>t</i> -Bu) ₃ ^b		143
		PPh ₃ , P(<i>p</i> -Tol) ₃ , ^j		145
		P(<i>m</i> -C ₆ H ₄ F) ₃		
	P(O- <i>o</i> -C ₆ H ₄ - <i>i</i> -Pr) ₃ ^o		PPh ₂ (<i>i</i> -Pr) ^b	148
	P(O- <i>o</i> -C ₆ H ₄ Ph) ₃ ^o			150
P(NMe ₂) ₃				152
		P(<i>t</i> -Bu) ₃ ^b	PPh ₂ (<i>t</i> -Bu) ^b	157
		PBz ₃ ^o	PPh ₂ C ₆ F ₅ ^b	158
		PCy ₃ ^h	PPh(<i>t</i> -Bu) ₂ ^b	160
	P(O- <i>t</i> -Bu) ₃			165
	P(O- <i>o</i> -C ₆ H ₄ - <i>t</i> -Bu) ₃ ^h			170
		P(neopentyl)		172
		P(<i>t</i> -Bu) ₃		175
		P(C ₆ F ₅) ₃		
	P(O-2,6-C ₆ H ₃ Me ₂) ₃ ^o			~180
		P(<i>o</i> -Tol) ₃		182
		P(mesityl) ₃ ^b		184
				190
				194
				212

^a From model measurements in ref 2 unless noted otherwise. ^b Previously unpublished value. ^c Based on a "sideways" phenyl ring with $\theta/2 = 65^\circ$.

^d Values given are for half of the chelate assuming PMP angles in $M[R_2P(CH_2)_nPR_2]$ of 74, 85, or 90° for $n = 1, 2$, or 3, respectively. ^e Reference 250.

^f Reference 9. ^g Increased 2° from the value in ref 2 because PBu₃ should not be smaller than PEt₃. ^h Value based in part on the degree of substitution of CO from Ni(CO)₄ (Figure 9).

APPENDIX C. Cone Angles^a for Ligands not Bound by a Group 5 Atom

X ^b	R	Other	Cone angle, deg	X ^b	R	Other	Cone angle, deg
H			75	Br ^d			105
	Me		90	I			107
F			92		<i>t</i> -Pr		114
		CO, CN, N ₂ , NO	~95°		CH ₂ CMe ₃ ^e		120
		COCH ₃	100		<i>t</i> -Bu		126
Cl	Et		102			Cp	136'
	CH ₂ Ph		104				

^a Based on a metal covalent radius of 1.32 Å. ^b Calculated using the covalent and van der Waals radii (Å) of the CPK models: H (0.33, 1.00), F (0.57, 1.35), Cl (0.99, 1.80), Br (1.14, 1.95), and I (1.35, 2.15). ^c The covalent and van der Waals radii of the CPK-C≡ atom lead to a cone angle of 113°. This must be an overestimate since group 6 M(CO)₆ complexes are very stable. A θ for CO slightly larger than 90° is suggested by the angles in Mn₂(CO)₁₀ (Table VIII) and HMn(CO)₅ (structure 102). ^d The maximum and minimum half angles are 85 and 40°. ^e Essentially the same cone angle was obtained for CH₂SiMe₃, assuming a 0.96 Å covalent radius for Si. ^f An M-Cp distance of 2.03 Å was assumed, as reported for CpWC(CF₃C₂CF₃)₂ by J. L. Davidson, M. Green, D. W. A. Sharp, F. G. A. Stone, and A. J. Welch, *Chem. Commun.*, 706 (1974).

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